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Soluble Salts in Porous Materials:
Evaluating Effectiveness of their Removal

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1. INTRODUCTION

Soluble salts are generally considered to be the single most important deterioration factor for porous materials. Salt decay leads to both aesthetic damage, through the formation of efflorescences, and physical damage, through the disaggregation of the material. A significant body of literature exists which attempts to explain and quantify the results of soluble salt decay. However, the manner in which salts crystallize within the pores of a material is yet to be elucidated. Furthermore, no agreement exists on the mechanisms ruling this process. The complexity of the problem increases dramatically when combinations of different salts are present which is the case for building materials.

Although difficult and seldom complete, removal of the soluble salts is the most obvious conservation treatment for porous materials facing salt decay. While it is easy to quantify the amount of salts within a building sample, no good method exists for accurately quantifying the distribution and the total amount of soluble salts in an entire building. Lower regions of a wall will have different types and concentrations of salts than upper portions.¹ Similar differences can also be observed from the exterior wall surfaces to the interior of the walls.² So far only destructive techniques can be used to determine salt concentrations. Since the quantity and mix of salts throughout a building

¹ Andreas Arnold. "Rising Damp and Saline Minerals." in *Fourth International Congress on the Deterioration and Preservation of Stone Objects July 7-9, 1982 Proceedings*, ed. K. L. Gaur and J. A. Gwinn (Louisville: University of Louisville, 1982), p. 11-28

² Fernand Auger. "World Limestone Decay under Marine Spray and Conditions." in *The Conservation of Monuments in the Mediterranean Basin The Influence of Coastal Environment and Salt Spray on*

concerns. As a result, the effectiveness of any salt removal method from an actual building or object can only be estimated, even if a large number of samples had originally been taken to quantify the salt content. Although many publications discuss the methodology and the amount of salt removed, not knowing the original amount present leaves open the question of the treatment's effectiveness.

This study focuses on the removal of soluble salts from two sets of ceramic tiles with different porosities containing known amounts of salts. The tiles had been impregnated with individual salts or their combinations. The individual salts were sodium chloride, sodium sulfate, or gypsum, and the combinations were mixtures of sodium chloride with either sodium sulfate or gypsum. These mixtures were chosen since they are the most frequently found in both masonry materials and archaeological ceramics. The salts had been introduced into the tiles by immersion in saturated solutions, and the amount of salts deposited in them determined gravimetrically.³

The study assesses the efficiency of salt removal by either immersion procedures or poultices. The tiles were totally immersed in different amounts of deionized water for different lengths of time or poulticed with absorbent clays. Absorbent clays in poultices is a common desalination technique for buildings, as well as, for especially fragile ceramic objects. Conductimetric measurements were used to monitor the amount of salts removed. Immersion procedures are most applicable to discrete removable objects, such as archaeological ceramics or removable architectural elements. The evaluation of the

Limestone and Marble Proceedings of the 1st International Symposium Bari 7-10 June 1989, ed. Fulvio Zezza (Brescia, Italy: Grafo, 1990), p. 65-69.

removed salts using the described desalination techniques contributes fundamental information regarding the effectiveness of these procedures for different salts and their mixtures. Since the total amount of salts in each tile was known, it was possible to evaluate the actual effectiveness of the removal procedure from a body of a given porosity. This information can also serve as a guideline to estimate the remaining salt content in a given object of similar porosity after desalination with one of these techniques.

³ A. Elena Charola and Sara Nunberg. "Soluble Salts in Ceramic Bodies: Deterioration Due to Minimal Changes in Relative Humidity." Manuscript to be submitted to *Studies in Conservation*.

2. DECAY MECHANISMS DUE TO SALT CRYSTALLIZATION

2.1 MECHANISMS OF DECAY: MECHANICAL

Despite numerous studies, no conclusive explanation of how salts damage porous materials exists.⁴ Much of the literature relies on the explanation that as a salt crystallizes it fills a pore. When there is no more space for a salt in a pore to crystallize, it exerts pressure on the pore walls. This deterioration mechanism is said to increase when a salt hydrates easily. The increase in volume resulting from the hydration of a salt creates pressure which damages the interior pore structure of the material. The earliest explanations state that for salts such as sodium sulfate or magnesium sulfate, which can exist in a hydrated form, cause damage: "due to the increase in volume, as they get a higher degree of hydration. This increase in volume produces cracking of the stones or their components."⁵ While the 314% increase in size of sodium sulfate decahydrate is significant, attributing this as the cause of deterioration assumes "a solid state or insitu conversion of Na_2SO_4 to $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. It is difficult to imagine how orthorhombic Na_2SO_4 can be converted to monoclinic $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ by a solid state reaction."⁶

⁴ Michael Steiger and Anke Zeunert. "Crystallization Properties of Salt Mixtures: Comparison of Experimental results and Model Calculations." in *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone Berlin, 30 September – 4 October 1996*, ed. Joseph Riederer (Berlin: Moller Druck und Verlag, 1996), p. 535.

⁵ Andreas Arnold. "Soluble Salts and Stone Weathering." in *The Conservation of Stone I Proceedings of the International Symposium Bologna, June 19-21, 1975*, ed. by R. Rossi-Manaresi (Bologna: Centro Per La Conservazione Delle Sculture All'Aperto, 1976), p. 133.

⁶ S. Chatterji, P. Christensen, and G. Overgaard. "Mechanisms of Breakdown of Natural Stones Caused by Sodium Salts." in *Deterioration and Preservation of Stones 3rd International Congress Venezia 24-2 10 1979* (Padova: Universita degli Studi di Padova, 1979), p. 131.

Recent work established that the dehydration of the decahydrate proceeded in a multi-step fashion.⁷ This was confirmed by environmental scanning electron microscopy through the observation of the in situ crystallizing sodium sulfate, its hydration, and its dehydration.⁸ The study also confirms that the hydration of sodium sulfate to the decahydrate is much slower and more complex than previously thought. Explanation relying solely on the expansion of the crystal due to hydration, ignores the fact that salts that do not have or can not easily convert to different hydration levels can also cause severe damage. Examples of these types of salts are sodium chloride and gypsum.⁹

It has been recently proposed that the volumetric increases resulting from changes in the concentration of the salt/water system, produce stress at the systems surface boundary by the hydraulic pressure induced by the liquid medium.¹⁰ Using this explanation, it becomes clear how cyclical crystallization of sodium chloride which dissolves easily in little water could cause severe damage. While both of these two

⁷ A. Elena Charola and Johannes Weber, "The Hydration-Dehydration Mechanism of Sodium Sulphate," in *Proceedings of the 7th International Congress on Deterioration and Conservation of Stone, Lisbon, Portugal 15-18 June, 1992*, ed. J. Delgado Rodrigues (Lisbon: Laboratorio Nacional de Engenharia Civil, 1992), p. 581-590.

⁸ Eric Doehne, "In Situ Dynamic of Sodium Sulfate Hydration and Dehydration in Stone Pores: Observation at High Magnification Using the Environmental Scanning Electron Microscope," in *Stone and Monuments: Methodologies for the Analysis of Weathering and Conservation Proceedings of the 3rd International Symposium Venice 22-25 June 1994*, ed. Vasco Fassina et al. (Venice: Soprintendenza ai Beni Artistici e Storici di Venezia, 1994), p. 143-150.

⁹ Antonio Moropoulou and Panagiotis Theoulakis, "Conditions Causing Destructive NaCl Crystallization into the Porous Sandstone, Building Material of the Medieval City of Rhodes," in *The Conservation of Monuments in the Mediterranean Basin Proceedings of the 2nd International Symposium Geneva, 19-21 November 1991*, ed. Dancielle Decrouez et al. (Geneva: Museum d'Histoire Naturelle and Musée d'Art et d'Histoire, 1991), p. 493-499; and K. Zelinder, "New Aspects of Decay Caused by Crystallization of Gypsum," in *Conservation of Stone and Other Materials Volume One Causes of Disorders and Diagnosis Proceedings of the International RILEI UNESCO Congress Paris June 29 - July 1, 1993*, ed. M. J. Thiel (London: E & FN Spon, 1993), p. 107-114.

¹⁰ Joseph Pühringer, "Deterioration of Materials by Hydraulic Pressure in Salt/Water Systems – An Outline Model," in *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone*

theories may explain in part the damage soluble salts cause, a complete understanding of the decay mechanism of salt crystallization awaits more research. Further, the scenario is complicated significantly when different salts coexist in various combinations and concentrations. Little of the research takes into account the actual conditions within a pore. Most ignore the effect of capillary condensation and the different susceptibility of variously sized pores to salt damage.

2.2 MECHANISMS OF DECAY: OTHER

A. B. Paterakis suggests that calcium sulfate and calcium carbonate can cause the chemical disintegration of some ceramics by the "devitrification of glazes and highly fired ceramic bodies by the leaching of alkalis and dissolution of colloidal silica."¹¹

While some salts may lead to the chemical decay of materials, experimentation using bricks illustrates that the damage is negligible when compared to the mechanical decay caused by soluble salts.¹² Because the primary damage caused by soluble salts is in the form of mechanical decay, additional research on this topic would be most useful to the field of building conservation.

In addition to direct decay, salts may increase the rate and severity of other decay mechanisms. Research conducted by Lubica Wessman shows that bricks containing

Berlin, 30 September – 4 October 1996, ed. Joseph Riederer (Berlin: Moller Druck und Verlag, 1996), p. 550.

¹¹ A. B. Paterakis, "The Deterioration of Ceramics by Soluble Salts and Methods for Monitoring Their Removal," in *Recent Advances in the Conservation and Analysis of Artifacts* (London: Institute of Archaeology, 1987), p. 70.

¹² A. E. Charola and R. J. Koestler, "The Action of Salt-Water Solutions in the Deterioration of the Silicio-Aluminate Matrix of Bricks," in *Il Mattone di Venezia: Contributi Presentati al Concorso di Idee su Patologia, Diagnosi e Terapia del Mattone di Venezia: Ateneo Veneto, Venezia, 29 Ottobre 1982*, (Venezia: Comune di Venezia, 1982), p. 67-76.

salts, especially sodium chloride, are more susceptible to freeze-thaw damage.¹³ Besides increased susceptibility to freeze-thaw deterioration, the change in pore size may lead to an increased susceptibility to capillary rise or capillary condensation. If a relatively insoluble salt, like gypsum, is found in a porous material, the opposite may happen. The open porosity may decrease as a result of pores being blocked by the salt. A resultant decrease in water vapor transmission can then lead to accelerated damage of the material.¹⁴ Finally, the hygroscopic nature of salts leads to a decrease in the drying rate of porous materials, and masonry walls will retain more water, further increasing damage.

2.3 EFFECT ON CONSERVATION TREATMENTS

In addition to increasing the rate of decay of porous materials, soluble salts can interfere with conservation treatments. For example, as described above, less soluble salts, such as gypsum, block surface pores reducing the absorption of consolidants and water repellents. Further, experience and laboratory tests have indicated a significant decrease in the hydrolysis rate of methyl-trimethoxysilane consolidants within porous materials contaminated with sodium sulfate and magnesium.¹⁵

¹³ Lubica Wessman, "Studies of Salt-Frost Attack on Natural Stone," in *Proceedings of the 8th International Congress on Deterioration and Conservation of Stone Berlin, 30 September – 4 October 1996*, ed. Joseph Riederer (Berlin: Moller Druck und Verlag, 1996), p. 563-571.

¹⁴ L. Franke and J. Grabau, "Transport of Salt Solutions in Brickwork," in *Conservation of Historic Brick Structures Case Studies and Reports of Research*, ed. N. S. Baer, S. Fitz, and R. A. Livingston (London: Donhead Publishing Ltd., 1998), p. 167-172.

¹⁵ Rakesh Kumar and Clifford A. Price, "The Influence of Salts on the Hydrolysis and Condensation of Methyl-Trimethoxysilane," in *Stone and Monuments: Methodologies for the Analysis of Weathering and Conservation Proceedings of the 3rd International Symposium Venice 22-25 June 1994*, ed. Vasco Fassina et al. (Venice: Soprintendenza ai Beni Artistici e Storici di Venezia, 1994), p. 861-865.

2.4 DAMAGE

While the mechanisms of salt decay are not clearly understood, the damage which salts cause is clear. Salts may crystallize either as efflorescence or subflorescence. If the drying rate is slower than the rate of salt solution migration to the surface of the material, then the salts crystallize on the surface. This phenomena is known as efflorescence.¹⁶ While efflorescence does not actively deteriorate the porous body, it can have a dramatic aesthetic impact on the building, compromising its visual integrity.

Subflorescence occurs when the solution in a wall migrates slower than the rate of evaporation resulting in the crystallization of salts just below the surface occur. A major cause of damage, subflorescence is responsible for the flaking, spalling, sugaring, and pitting of porous building materials. Further, in the instance of glazed ceramics, subflorescence results in the loss of cohesion of the pigments and glazes.

Arnold proposes a model for walls where rising damp causes the transportation of the salts. He divides walls into four zones: A, B, C, and D according to the difference in deterioration caused by salt.¹⁷ In this model, Zone A is closest to the soil and represents a wall height up to approximately 0.5 meters. It contains salts with the lowest solubility including calcium carbonate, magnesium carbonate, and calcium sulfate. Zone A shows very few signs of deterioration, when deterioration is present, it is limited to flaking.

Zone B represents the height of the wall between 0.5 and 1 meter. Zone B contains moderately soluble salts including magnesium sulfate, potassium nitrate, sodium

¹⁶ R. Rossi-Manaresi and A. Tucci, "Pore Structure and the Disruptive or Cementing Effect of Salt Crystallization in Various Types of Stone," *Studies in Conservation* Vol. 36 (1991): p. 53.

¹⁷ Andreas Arnold. "Rising Damp and Saline Minerals," p. 11-28.

sulfate, and, in alkaline environments, sodium carbonate. This zone generally has significant efflorescence, and the damage is the most severe. Physical decay in Zone B includes the typical damage associated with soluble salts: granular disintegration, alveolar weathering, and flaking.¹⁸

Higher on the wall, between 1 and 3 meters above the ground, is Zone C. This zone contains the most soluble salts, including sodium chloride, potassium chloride, sodium nitrate, calcium nitrate, and magnesium nitrate. While no clear signs of deterioration exist in this zone, the wall appears darker due to increased amounts of water, a result of the hygroscopic nature of salts. The darkened areas may appear spotted indicating a non-homogeneous distribution of salts. Further, the darkness, i.e. amount of water, will vary depending on the temperature and relative humidity.

Zone D refers to the height above where capillary rise is a problem. It represents the sound wall. This division only serves as a rough guide. There may be substantial differences between the height of each of these zones.¹⁹

2.5 ORIGINS OF SOLUBLE SALTS

The origin of salts in porous material is extremely complex. Furthermore, once inside a porous material, the different ions can recrystallize as different salts. The following provides only a brief outline of the problem; since, the sources must be analyzed on an individual building basis. Defining factors for the type of salts to be found include the geographic location of a building, its environment, and its past history.

¹⁸ Andreas Arnold. "Rising Damp and Saline Minerals." p. 11-28.

¹⁹ Arnold, Andreas. "Rising Damp and Saline Minerals." p. 11-28.

Appendix A provides a list of common salts found in historic buildings and their solubilities.

Table 1: Salt Concentration in Sea Water²⁰

| Salt | Atlantic Ocean grams / liter | Mediterranean Sea grams / liter |
|-------------------|---|--|
| NaCl | 28.14 | 30.76 |
| KCl | 0.69 | 0.66 |
| MgCl ₂ | 3.44 | 3.74 |
| CaSO ₄ | 1.42 | 1.64 |
| MgSO ₄ | 2.28 | 2.39 |

Sea water is one of the most commonly cited sources of soluble salts in coastal historic buildings. Table 1 provides the concentration of salts in the Atlantic Ocean and the Mediterranean Sea. The salts found in sea water can infiltrate a building either through rising damp or deposition on the wall surface through salts in the air. The sea is the leading source of chloride salts and may provide substantial amount of sulfate salts. The sea provides a continual source of salts for buildings in its vicinity.

In northern climates, sodium chloride and calcium chlorides can enter into buildings as a result of deicing salts. These salts reduce the freezing point of water, and thus melt the snow and ice. The resulting salt solution is absorbed by capillaries into the wall.

²⁰ Fernand Auger. "World Limestone Decay under Marine Spray and Conditions." p. 65-69.

Another important salt source, atmospheric pollution, either as dry deposition or acid rain, may introduce sulfate or nitrate ions into a building. Sulfate ions can react with sodium ions, deposited by sea water or from some other source, to form the damaging sodium sulfate. Acid rain may also chemically attack calcareous building materials to form gypsum, often found as a black crust. Nitrates only produce highly soluble salts with sodium, potassium, or calcium ions. These can enhance microbiological activity.

Warmer climates promote microbiological growth. These growths can increase sulfate, nitrate, or nitrite deposition on a building surface. Nitrates may also be present in ground soil as a result of decaying organic material.

In many cases, salts are already present in the original building materials, such as sodium sulfate in underfired bricks or alkali sulfates in concrete. They only need water to mobilize and cause damage. Sand obtained from coastal regions for mortar can transfer sea salts into a building during original construction.²¹

Salts may have also been intentionally added to original building materials. Research from the NATO-CCMS pilot study on brick conservation suggests that sodium chloride may have been deliberately added during the brick-making process in some areas.²² Early twentieth century sources suggest the use of soluble metallic salts as colorants for glazed terra cotta. Problems with these colorants were recognized even at the time: "we have found in actual practice that our greatest difficulty with soluble salt

²¹ R. P. J. van Hees. "Damage Caused by Salts to Curacao-Monuments." in *Structural Repair and Maintenance of Historical Buildings II Proceedings of the Second International Conference Held in Seville, Spain 14-16 May 1991*, ed. C. A. Brebbia et al. (Boston, Computational Mechanics Publications, 1991), p.141-155.

solutions was the fact that they frequently loosened the glaze coat on which they were applied."²³

Incompatible materials placed adjacent to each other may also result in damage from soluble salts. For example, when limestone is placed above terra cotta or siliceous stones such as sandstone and granite, the calcium bicarbonate and calcium sulfate may leach into the ceramic and cause blistering and exfoliation.²⁴

Soluble salts may exist in a building as a result of its use. In an extreme example, a building used for the processing of mined salt was found to be contaminated with sodium and potassium chloride.²⁵ In another example, at Colonial Williamsburg, the source of the sodium chloride deteriorating a brick building was determined to result from its use as a smokehouse.²⁶

Modern interventions into historic structures may also introduce soluble salts. The use of Portland cement as a replacement mortar for masonry buildings may lead to the development of damaging alkaline salts, commonly found in concrete.²⁷ Previous

²² Richard Livingston, Stephen Fitz, and Norbert S. Baer, "The NATO-CCMS Pilot Study on the Conservation of Brick Monuments," in *The Fifth North American Masonry Conference, University of Illinois at Urbana-Champaign June 3-6, 1990* (Boulder: Masonry Society, 1990), p. 805-812.

²³ A. Lee Bennett, "The Use of Overglazes for Polychrome Terra Cotta," *Journal of the American Ceramics Society*, Vol. 9, No. 4 (April 1926), p. 186.

²⁴ John Fidler, "Fragile Remains: An International Review of Conservation Problems in the Decay and Treatment of Architectural Terracotta and Faience," in *Architectural Ceramics: Their History, Manufacture and Conservation A Joint Symposium of English Heritage and the United Kingdom Institute for Conservation 22-25 September 1994* (London: James, 1996), p. 14.

²⁵ S. Herppich, "Bricks Under the Influence of Huge Salt Inmissions Building of a Thuringian Potash Mine," in *Conservation of Historic Brick Structures Case Studies and Reports of Research*, ed. N. S. Baer, S. Fitz, and R. A. Livingston (London: Donhead Publishing Ltd., 1998), p. 477-484.

²⁶ Richard A. Livingston and Thomas H. Taylor Jr., "Diagnosis of Salt Damage at a Smokehouse in Colonial Williamsburg," *APT Bulletin* Vol. XXIII No. 3 (1991): p. 3-12.

²⁷ Andreas Arnold, "Soluble Salts and Stone Weathering," in *The Conservation of Stone I Proceedings of the International Symposium Bologna, June 19-21, 1975*, ed. R. Rossi-Manaresi (Bologna: Centro Per La Conservazione Delle Sculture All'Aperto, 1976), p. 133-135.

conservation treatments, such as the cleaning of architectural ceramics with hydrochloric acid, may result in the eventual formation of soluble salts.²⁸

Archaeological ceramics suffer deterioration from the same salts as buildings. Their source is most often the ground soil where they were buried. Salts can also exist as a result of the object's original use. Further, many objects on display in museums, stored in hardwood cases, have developed efflorescence of acetate salts as a result of fumes released by the wood.

Clearly, the first crucial step in conserving a building or an object suffering from salt decay is a careful analysis of the salt present and the identification of its source. Once the source of soluble salts is known, the conservator will be able to make adequate measures for their elimination.

²⁸ Clifford Price, "Stone-decay and Preservation." in *Masonry Conservation and Cleaning Handbook* ed. Keith Blades et al. (Ottawa: Association For Preservation Technology, 1985). p. 128-131.

3. CONSERVATION

The first step in the conservation of salt-contaminated materials is the identification of the types and sources of salts, and their quantification. Second, further deterioration should be reduced by limiting the water sources or controlling the crystallization of the salts. Finally, if possible, the salts should be removed.

3.1 IDENTIFICATION OF SALTS

The first step to a proper conservation treatment of salt contaminated materials is to identify the salts, a relatively easy step. Microchemical spot tests are the simplest and most economic method for the identification of the specific ions present in the soluble salts. Polarized light microscopy can be further used to determine their actual crystal form and nature. If more information is required analytical techniques such as x-ray diffraction or mineral characterization can be used.

Following salt identification, quantification of the salts could serve to determine the severity of the problem. A simple method of quantification is to soak a ground sample in deionized water and then measure the difference in weight of the dry sample before and after, to obtain a percentage of the total salts. Titrations or ion chromatography can quantify the actual amount of ions present in the resulting solution.

Since salt content is seldom homogenous throughout a wall, as suggested by Arnold's analysis, a suitable number of samples must be taken to get an indication of the salt content in each portion of the wall. Core drill samples should be taken across the wall, at various heights, and at various depths.

Some preliminary work on the smokehouse at Colonial Williamsburg suggests that nondestructive testing using neutron probe can provide reliable results about the salt content, but this technique awaits a clear set of standards and methodologies.²⁹

Once a clear picture of the types and quantity of salts is obtained, a determination of the source of the salts should be made. Soil samples near the structure should be taken to determine the salts present in the soil. Location, environment, history of use, and conservation history should be analyzed. If the salt concentration follows the basic model outlined by Arnold, then capillary rise of ground water is most likely the source of the salts. Atmospheric pollution is probably the source of salts found on the surface. Uniform salt concentration indicates that the building materials may have contained salts originally, or a previous conservation treatment could have left its scar.

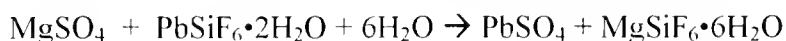
3.2 IMMOBILIZATION OF SALTS

Salts are only a problem if they have a water supply and can continue to move and crystallize throughout a building. If the original source of salts no longer exists, no conservation treatment may be necessary, although removal of the salts may be desirable. Often the source of water can be eliminated by routine maintenance, such as cleaning and repairing gutters. If the salts enter the building from the soil through capillary rise of ground moisture more drastic conservation action must take place. The most effective conservation solution so far is to create an impermeable barrier which can stop water infiltration. A mechanical insertion of an impermeable layer, such as metal, has

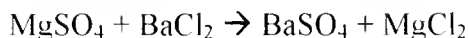
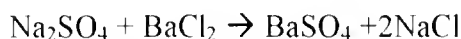
²⁹ Richard A Livingston and Thomas H. Taylor Jr., "Diagnosis of Salt Damage at a Smokehouse in Colonial Williamsburg," *APT Bulletin* Vol. XXIII No. 3 (1991): p. 3-12.

successfully been used to stop water infiltration through capillary rise in some historic buildings in Northern Europe.³⁰ Alternatively, chemical barriers such as bitumen emulsions, epoxies, and polyeurathanes can also be used.³¹ Both physical and chemical interventions require destructive intervention to a building. If water is penetrating through the vertically exposed surface of the wall either through rain or condensation, a water repellent could minimize its affect.

Another proposed solution to reduce the mobility and damage, although not recommended, is to form insoluble compounds from the salts. For this purpose, lead fluosilicate has been used. The lead reacts with the anion, either the sulfate ion or the chloride ion, to create less soluble lead sulfate or lead chloride. Magnesium or sodium fluosilicate remain. The reactions are:



While still moderately soluble, these fluosilicate are less destructive than the sulfate salts. Alternatively, barium chloride may be injected into the contaminated wall. The reaction is:



³⁰ G. Dingethal, P. Andriolo-Stagno, and H. Weber, "Patologia e Cura Dimurature in Mattoni Danneggiate Dall'Umidita' e Dalla Presenza di Sali," in *Il Mattone di Venezia : Contributi Presentati al Concorso di Idee su Patologia, Diagnosi e Terapia del Mattone di Venezia : Ateneo Veneto, Venezia, 29 Ottobre 1982*, (Venezia: Comune di Venezia, 1982), p. 397-435.

While this method eliminates the destruction caused by sulfate salts, it still leaves the chloride salts.³² Chemical conversion of damaging soluble salts to insoluble compounds may reduce damage; however, damage will continue as a result of the remaining salts. Also, the effect of this treatment will dramatically change other characteristics of the building material, such as water vapor transmission. These changes may lead to different decay mechanisms.

3.3 DESALINATION: BUILDINGS

Once intervention has stopped the addition of new soluble salts into a building, an attempt to desalinate the walls may begin. The effectiveness of desalination is difficult to evaluate; hence, further research is necessary to determine how to assess it. Adequate desalination varies with each type of material depending on its environment. For instance, in brick, a sodium chloride content of less than 1.5% by weight may not lead to any damage.³³ In contrast, a chloride content of less than 0.4% in reinforced concrete can cause significant damage due to iron corrosion.³⁴ Further research must be conducted to obtain an idea of what a safe salt content is for each material.

Efflorescence is easier to remove than subflorescence. The least invasive technique to remove efflorescence is simply to brush the salts off of the surface when it appears after crystallization. This technique works best when the salts are loosely

³¹ G. Dingethal, P. Andriolo-Stagno, and H. Weber, "Patologia e Cura Diminuzione in Mattoni Danneggiati Dall'Umidità e Dalla Presenza di Sali," p. 397-435.

³² Helmut Weber, *Mauerfeuchtigkeit: Ursachen und Gegenmaßnahmen*, 2nd Ed. (Sindelfingen, Germany: Expert Verlag, 1984), p. 102-109.

³³ Richard A. Livingston and Thomas H. Taylor Jr., "Diagnosis of Salt Damage at a Smokehouse in Colonial Williamsburg," *APT Bulletin* Vol. XXIII No. 3 (1991): p. 7.

attached to the original material. Brushing off the salts removes some of the salts from the building, ensuring that they do not reenter the system. While this minimal intervention treatment can improve the aesthetic problems caused by salts, some will remain within the porous material. These remaining salts can continue to crystallize and cause damage.

Another technique used to desalinate walls is simply to flush the surface repeatedly with water.³⁵ In this technique, a fine mist of water is sprayed over the wall, which is then allowed to dry. The treatment is repeated until little new efflorescence appears. Flushing a wall with water supposedly brings the salts from within the wall to the surface. This technique, however, may lead to a rapid deterioration due to increased salt mobility during desalination. Further, if too much water is used or the rate of evaporation is too slow, the salts may be driven further into the wall. If this happens, the salts will remain in the wall continuing to cause damage and making future desalination efforts more difficult.³⁶

Poulticing is a second common desalination technique of salt-contaminated masonry. In this process, a material which dries slowly - either an expansive clay such as attapulgitite or bentonite, or a paper poultice - is placed on a dampened wall. Since the drying rate is slower than the rate the salt solution moves to the surface, efflorescence

³⁴ T. P. Lees. "Deterioration Mechanisms." in *Durability of Concrete Structures: Investigation, Repair, Protection*, (New York: E & F. N. Spon. 1992). p. 36.

³⁵ V. Fassina, R. Arbizzani, A. Naccari, and M. Favaro. "Brick Masonry of the Crypt of San Marco Basilica." in *Conservation of Historic Brick Structures Case Studies and Reports of Research*, ed. N. S. Baer, S. Fitz, and R. A. Livingston. (London: Donhead Publishing Ltd., 1998). p. 407-426.

³⁶ J. L. Heiman. "Rising Damp and Salt Attack in Old Masonry." in *Proceedings of the 7th International Brick Conference Melbourne Australia 17-20 February 1985*, ed. Tom McNelly and John C. Scrivener (Melbourne: University of Melbourne, 1985). p. 240.

occurs. Instead of forming on the surface of the wall, the salts crystallize in the poultice. After the poultice dries, it is removed along with the salts. Like desalination by washing, the initial wetting of the surface during a poultice treatment may drive the salts deeper into the wall, leading to continued salt decay and making future desalination treatments more difficult.³⁷

To decrease the transportation of salts further into the masonry, a technique known as injection poulticing has been used.³⁸ This technique utilizes pressure transport to desalinate porous materials. A pressure gradient is formed as water injected into the middle of the wall and is forced out through the faces. The technique differs from traditional poulticing in that holes are drilled into the mortar joints of a wall to provide a constant water supply to the center of the wall. A poultice of expansive clay or paper is applied to the wall surface. The rate of transportation by capillary movement to the poultice is greater than the rate of evaporation from the poultice. As a result, the salts crystallize within the poultice; and, when the poultice is removed, the salts are removed with it. Research has indicated injection poulticing successfully removes the salts from the wall in one to four weeks.³⁹ While this solves the problem of pushing the salts further into the wall, the dampness which injection poulticing creates in the wall may lead to other types of damage.⁴⁰

³⁷ P. Friese and A. Protz, "Desalination of Brickwork and Other Porous Media," in *Conservation of Historic Brick Structures Case Studies and Reports of Research*, ed. N. S. Baer, S. Fitz, and R. A. Livingston (London: Donhead Publishing Ltd., 1998), p. 337.

³⁸ P. Friese and A. Protz, "Desalination of Brickwork and Other Porous Media," p. 335-345.

³⁹ P. Friese and A. Protz, "Desalination of Brickwork and Other Porous Media," p. 335-345.

⁴⁰ P. Friese and A. Protz, "Desalination of Brickwork and Other Porous Media," p. 335-345.

Architectural conservators have mainly utilized two long term desalination techniques: 1) sacrificial renders 2) electromigration. Plasters and stuccos have long been used in marine environments susceptible to salt damage as part of their original fabric. Conservators have adopted these sacrificial layers to slow salt damage in buildings, sometimes replacing those which have historically existed. In Venice, a highly permeable salt-resistant stucco has been used on fragile brickwork. Other times, they are added solely as a conservation treatment.⁴¹ A sacrificial stucco was one of four suggested conservation treatments for the salt contaminated smokehouse at Colonial Williamsburg, to shift the salt damage from the brickwork to the stucco.⁴²

This treatment poses some theoretical dilemmas. While adding a sacrificial stucco to a building historically stuccoed may create visual unity within the historic district, at Colonial Williamsburg a stucco would unalterably affect the aesthetic of the building. Further, a stucco can not easily be removed from a building without damage to the substrate.

In electromigration, also called electroosmosis, electrodes with an electric potential are inserted into the masonry. The electrodes may also be connected to the wall so as to create no damage. The speed of desalination is dependent on the electric potential applied and the specific characteristics of the materials. In a German brick

⁴¹ R. Crèvecoeur and H. H. O. Jahn. "The Preservation of Venetian Brickwork by the Use of a Salt Resistant and Vapour Permeable Plaster," in *Il Mattone di Venezia : Contributi Presentati al Concorso di Idee su Patologia, Diagnosi e Terapia del Mattone di Venezia : Ateneo Veneto, Venezia, 29 Ottobre 1982*, (Venezia: Comune di Venezia, 1982), p. 67-76.

⁴² Richard A. Livingston and Thomas H. Taylor Jr., "Diagnosis of Salt Damage at a Smokehouse in Colonial Williamsburg," *APT Bulletin* Vol. XXIII No. 3 (1991): p. 3-12.

house a potential of 50-60 volts was used.⁴³ In a Berlin church, after thirteen years, twenty-five kilograms of salt were removed using this technique. A further ten to twenty years are estimated before desalination is complete.⁴⁴ This technique requires a long time for complete desalination, and further tests are needed to determine its practical applicability to buildings. Although the technique has reported successful in some cases, the overall consensus considers this as a doubtful procedure for salt removal.

Occasionally, a portion of a building can be removed and treated as a discreet object.⁴⁵ After treatment it can be placed back into its building context. While not a very practical approach, this is sometimes the best approach, especially for significant portions of buildings, as desalination efficiency is greatly improved in movable objects as discussed below.

3. 4 DESALINATION: ARCHAEOLOGICAL CERAMICS

Complete desalination is easier to accomplish in discrete objects. Archaeological ceramics are often found contaminated with a high degree of soluble salts found in the soil. The desalination techniques that can be applied to archaeological ceramics are

⁴³ P. Friese and A. Protz. "Desalination of Brickwork and Other Porous Media." p. 341.

⁴⁴ P. Friese and A. Protz. "Desalination of Brickwork and Other Porous Media." p. 335-345.

⁴⁵ R. Crevecoeur. "The Desalination of a Marble Carved Seat in the Royal Palace, Amsterdam," in *Deterioration and Preservation of Stones 3rd International Congress Venezia 24-27 10 1979*. (Padova: Università degli Studi di Padova, 1979) p. 471-479; and Vasco Fassina, Rossana Arbizzani, and Andrea Naccari. "Salt Efflorescence on the Marble Slabs of S. Maria Del Miracoli Church: A Survey on Their Origin and on the Methodology of Their Removal," in *Proceedings of the 8th International Congress on deterioration and Conservation of Stone Berlin, 30 September – 4 October 1996*, ed. Joseph Riederer (Berlin: Moller Druck und Verlag, 1996), p. 523-534; and G. Galli, M. Matteini, A. Moles, and C. Manganelli. "Intervento di Desalinazione del Dossale di G. Di Rignano di Verona," in *Deterioration and Preservation of Stones: Proceedings of the 3rd International Congress* (Padova: Università degli Studi, Istituto di Chimica Industriale, 1982), p. 491-499.

based on the same ideas as building desalination. Generally, consolidation either proceeds or follows desalination treatments of ceramics.

Total immersion in deionized water is the most often used desalination technique for archaeological ceramics. On discovery, archaeological ceramics are generally saturated with saline water. In situ emergency conservation generally takes place to ensure that the salts do not immediately crystallize. For this purpose, the objects are generally kept in water until transported to a conservation laboratory. The water used for this immersion is often sea water, so that the osmotic pressure from desalination does not damage the object.⁴⁶

After arrival at a laboratory, the salt content of the water is slowly reduced. The water is then changed in stages: first to drinking water, then to rain water, and finally to deionized water. The process is often monitored using a conductance meter. Within this basic technique there are lots of variations. The most basic question is how much water should be used to desalinate. Conservators suggest that a large amount of water is needed for efficient desalination, from ten to fifteen milliliters of water per gram of object.⁴⁷ The second question conservators ask with regard to desalination by total immersion is: what is the necessary frequency to change the immersion water? Some sources suggest that

⁴⁶ Colin Pearson (ed.), *Conservation of Marine Archaeological Objects*, (London, Buttersworth, 1987), p. 257.

⁴⁷ J. Ciabach and Slawomir Skibinski, "Analyses of the Total Salt Content and Control of Salt Removal from Stone Historical Objects," in *The Conservation of Monuments in the Mediterranean Basin The Influence of Coastal Environment and Salt Spray on Limestone and Marble Proceedings of the 1st International Symposium Bari 7-10 June 1989*, ed. Fulvio Zezza (Brescia, Italy: Grafo, 1990), p. 325-328; and Alice Boccia Paterakis and Sarah Nunberg, "The Stabilization of Archaeological Pottery in an Excavation Study Collection through Relative Humidity and Through Desalination," in *Le Dessalement des Matériaux Poreux 7es Journées D'Etudes de La SFIIC Poitiers, 9- 10 Mai 1996*, (Champs-sur-Marne: SFIIC, 1996), p. 137-44.

the water should be continuously changed, while other sources state that changing water once or twice a day is sufficient.⁴⁸

Some sources erroneously suggest that agitation of the solution during desalination increases its efficiency.⁴⁹ While continuous stirring may increase the initial rate of desalination, it does not lead to any difference in the total amount of salt removed. The natural convection currents in a solution are strong enough to evenly disperse the salts. Further, continuous agitation can lead to erosion of the ceramic body.⁵⁰ Another suggestion, that has been made, is that increasing the temperature of the solution increases the rate of desalination.⁵¹ Again, this technique may lead to severe damage to the ceramics.

If a ceramic artifact is particularly friable, total immersion desalination may damage it. In these cases, desalination with an expansive clay or paper poultice is the preferred treatment. Poultices are applied the same way they are applied to buildings. First the object is wetted. Next a poultice is applied to all exposed surfaces. The poultice is allowed to dry, the time generally ranges from one to four days. The treatment is repeated until adequate desalination is achieved. Poulticing and the total immersion

⁴⁸ Alice Boccia Paterakis and Sarah Nunberg. "The Stabilization of Archaeological Pottery in an Excavation Study Collection through Relative Humidity and Through Desalination." in *Le Dessalement des Matériaux Poreux 7es Journees D'Etudes de La SFHIC Poitiers, 9- 10 Mai 1996.* (Champs-sur-Marne: SFHIC, 1996), p. 137-44; and "Soluble Salts and Deterioration of Archeological Materials." *Conserve O Gram* Number 6/5 (August 1998).

⁴⁹ Henry W. M. Hodges. "The Conservation Treatment of Ceramics in the Field." in *In Situ Archaeological Conservation: Proceedings of Meetings April 6-13, 1986 Mexico, 1987* (Los Angeles: Getty Conservation Institute, 1986), p. 145.

⁵⁰ J. L. Antunes. "Characterization of Portuguese 17th Century Tiles." in *Proceedings of the International Symposium on Ceramics in Architecture of the 8th CIMTEC-World Ceramics Congress and Forum on New Materials Florence, Italy June 28-July 1, 1984*, ed. P. Vincenzini (Faenza: L'Edinca, 1995), p. 658-660.

⁵¹ Henry W. M. Hodges. "The Conservation Treatment of Ceramics in the Field." p. 144-9.

processes can be used in conjunction with one another; a combination of the two has proven successful.⁵²

In the case of sun baked clay cuneiform tablets at the British Museum, the decision to fire the object at higher temperature was chosen before desalination. After firing, the tablets were desalinated by total immersion.⁵³ This approach ensured the protection of the most important information, the incised designs.

The use of electric potentials, as in electrodialysis, has been successfully applied to objects. As early as the 1930s the technique of electric migration had been used to desalinate ceramics.⁵⁴ Its particular usefulness comes in the ability to direct the movement of the salts. In one case, the salts on archaeological pottery displaced the pigmented surface. Through its appropriate application, this technique directed the salts away from the surface decoration, allowing the pigments to be set back in place and consolidated.⁵⁵

Recently, some questions about the need to desalinate objects placed in a museum have arisen, fearing that desalination will eliminate important organic information about the use and manufacture of ceramics.⁵⁶ To this end, the regulation of temperature and

⁵² P. Andrew Lins. "Technical Notes." in *Dutch Tiles in the Philadelphia Museum of Art*, ed. Jan Daniel van Dam and Pieter Jan Tichelaar. (Philadelphia: Philadelphia Museum of Art. 1984).

⁵³ A. Eric Parkinson. "The Preservation of Cuneiform Tablets by Heating to a High Temperature." *Museum News* (March 1, 1950): p. 6-8.

⁵⁴ Colin G Fink. "Incrustations on Porous Pottery: A New Method of Cleaning without Loss of Pigment." *Technical Studies* Vol. 2 (1933-4): p. 59-61.

⁵⁵ Colin G Fink. "Incrustations on Porous Pottery: A New Method of Cleaning without Loss of Pigment." p. 59-61.

⁵⁶ Denise Ling and Sandra Smith. "To Desalinate or not to Desalinate? That is the Question." in *Le Dessalement des Matériaux Poreux 7es Journées D'Etudes de La SFHC Poitiers, 9- 10 Mai 1996*, (Champs-sur-Marne: SFHC, 1996), p. 65-74.

relative humidity has recently gained popularity as a minimal conservation treatment.⁵⁷ Recent research, however, has shown that, salt can continue to cause damage even with minimal RH fluctuations below the critical RH.⁵⁸ Any decision to leave soluble salts in a archaeological ceramic, even if in a museum where the environment can be regulated, must be made cautiously.

Conservators have also increasingly discussed the question: what is a safe level of salt content? Each conservator has chosen a different ending point for desalination. In the total immersion technique, the suggested endpoint ranges from when the conductance of the water is less than 50 microsiemens to less than 1000 microsiemens.⁵⁹ It is necessary, however, to correlate this measurement with the total volume of solution. The necessary desalination, like in buildings, will depend on the characteristics and the condition of the material. More research must be undertaken to decide what level of desalination provides adequate removal of soluble salts.

⁵⁷ Alice Boccia Paterakis and Sarah Nunberg. "The Stabilization of Archaeological Pottery in an Excavation Study Collection through Relative Humidity and Through Desalination," in *Le Dessalement des Matériaux Poreux 7es Journees D'Etudes de La SFHC Poitiers, 9- 10 Mai 1996*, (Champs-sur-Marne: SFHC, 1996), p. 137-44.

⁵⁸ A. Elena Charola and Sara Nunberg. "Soluble Salts in Ceramic Bodies: Deterioration Due to Minimal Changes in Relative Humidity." Manuscript to be submitted to *Studies in Conservation*.

⁵⁹ J. Olive and C. Pearson. "The Conservation of Ceramics from Marine Archaeological Sources," in *Preprints of the Contributions to the Stockholm Congress 2- 6 June 1975 Conservation in Archaeology and the Applied Arts* (London: International Institute for Conservation, 1975), p. 63-68; and A. B. Paterakis. "The Deterioration of Ceramics by Soluble Salts and Methods for Monitoring Their Removal," in *Recent Advances in the Conservation and Analysis of Artifacts* (London: Institute of Archaeology, 1987), p. 67-73.

4. CHARACTERIZATION OF TILES

To test the relationship between porosity and desalination efficiency, two sets of tiles with different porosities were chosen. The porosities of these tiles are similar to the range frequently found in both architectural and archeological ceramics.

The red earthenware tiles (Munsell 10R Hue, 5 Value, 6 Chroma) used for the experimentation were manufactured by extruding a six by six centimeter slab of Ohio Red Art earthenware clay and slicing one and a half centimeter thick tiles from it. The earthenware tiles were fired at 800 °C (cone 015). After firing, the tiles measured an average of 5.7 centimeters by 5.6 centimeters by 1.4 centimeters and had an average weight of 71.61 grams. The tiles were friable and some formed hairline cracks along the edges during the experimentation.

The open porosity of the earthenware tiles was determined by twenty-four hour immersion (ASTM C67-97) in deionized water. A percent of the difference between dry and saturated weight was then calculated. The average weight gain of the four tested tiles was 17.7%, as shown in Table 2. During this test some disaggregation of the tiles occurred, but this had no significant effect on the calculations. The test was repeated with a five hour immersion in boiling water (ASTM C67-97). The average weight increase by this technique was 19.1%. During boiling immersion, three of the four tiles cracked and broke (Tiles A, C, and D). The test was continued, but these show a lower percent of weight gain than Tile B which remained intact. The pores were further characterized using optical microscopy to examine thin sections. A large number of

pores ranging from an area of 0.05 mm^2 to 0.0001 mm^2 were found. Appendix B lists the pore measurements in the earthenware tiles.

Table 2: Porosity of Earthenware Tiles

| Tile | Porosity percent weight gain | Boiling percent weight gain |
|---------|---------------------------------|--------------------------------|
| A | 16.9% | 18.3% |
| B | 17.9% | 20.2% |
| C | 18.7% | 19.3% |
| D | 17.1% | 18.7% |
| Average | 17.7% | 19.1% |

This distribution of large and medium sized pores make the tiles susceptible to salt decay. The high porosity is a result of a large pore area and the interconnectedness of the pores. The small difference in weight gained during the boiling immersion test shows that few very small pores exist.

The mineralogical characterization of the earthenware tiles was carried out by polarized light microscopy of thin sections (Figures 1-4). As expected, all of the identifiable minerals are silicates. Approximately 15% of the sample was small quartz grains. Identified by their sharp angular shape and 90° extinction angle, the quartz grains were well sifted with most having both a major and minor axis of 2.3×10^{-4} millimeters. There were also some very fine grains of quartz, only distinguishable at magnifications greater than 100 times. A minimal amount of plagioclase feldspars were identified by their lamellar twinning.

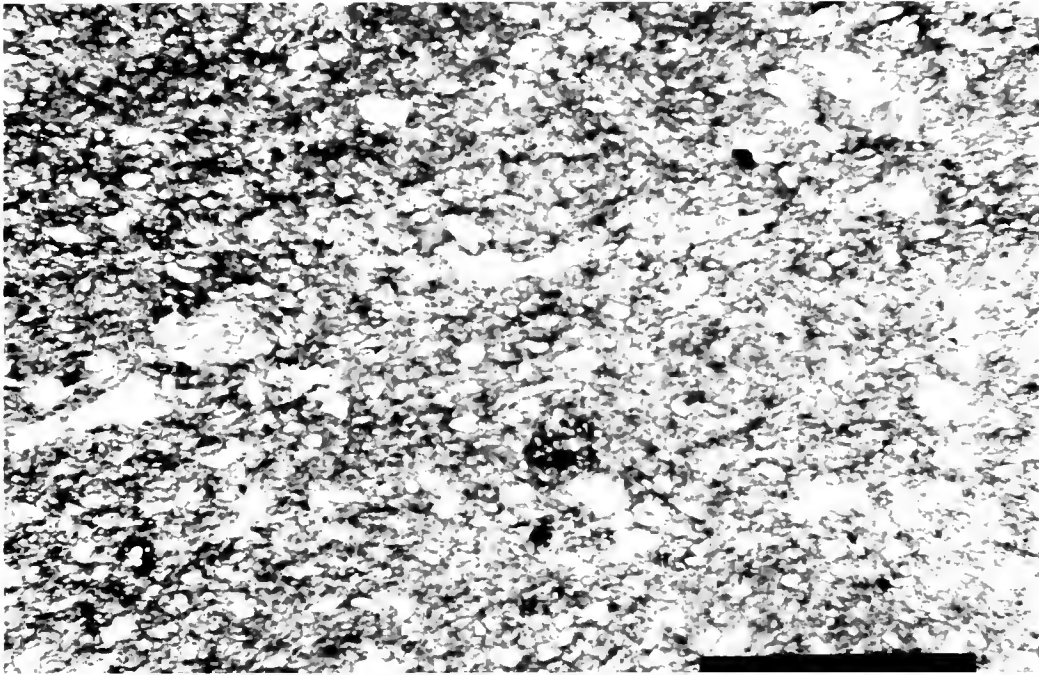


Figure 1: Photomicrograph of Earthenware Tile Thin Section in Transmitted Light (Magnification 25x).

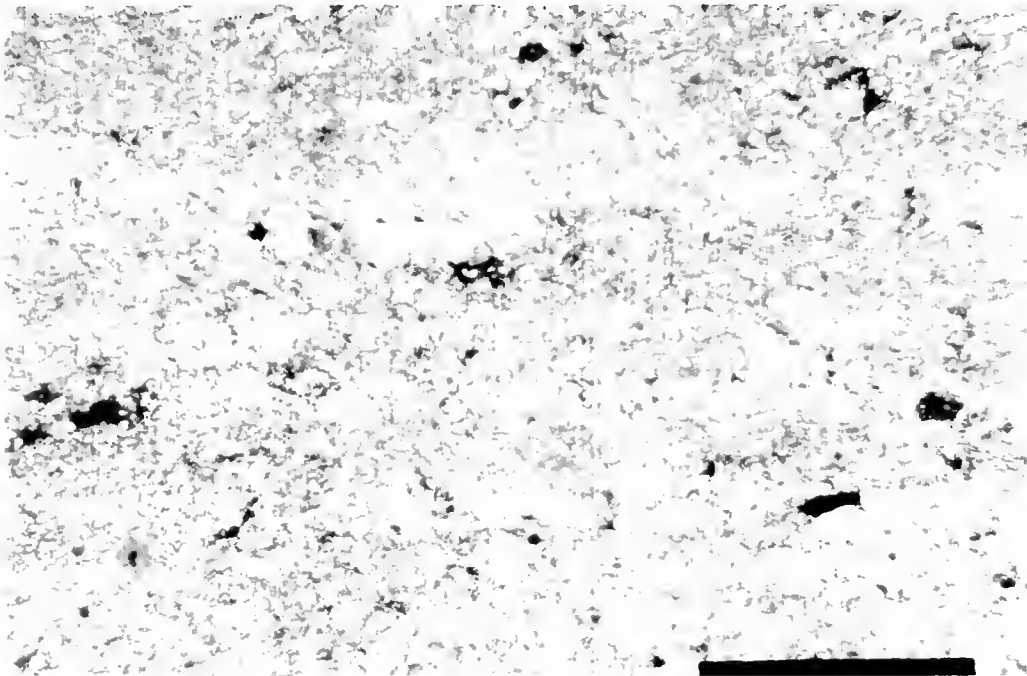


Figure 2: Photomicrograph of Earthenware Tile Thin Section under Cross Polarized Light (Magnification 25x).

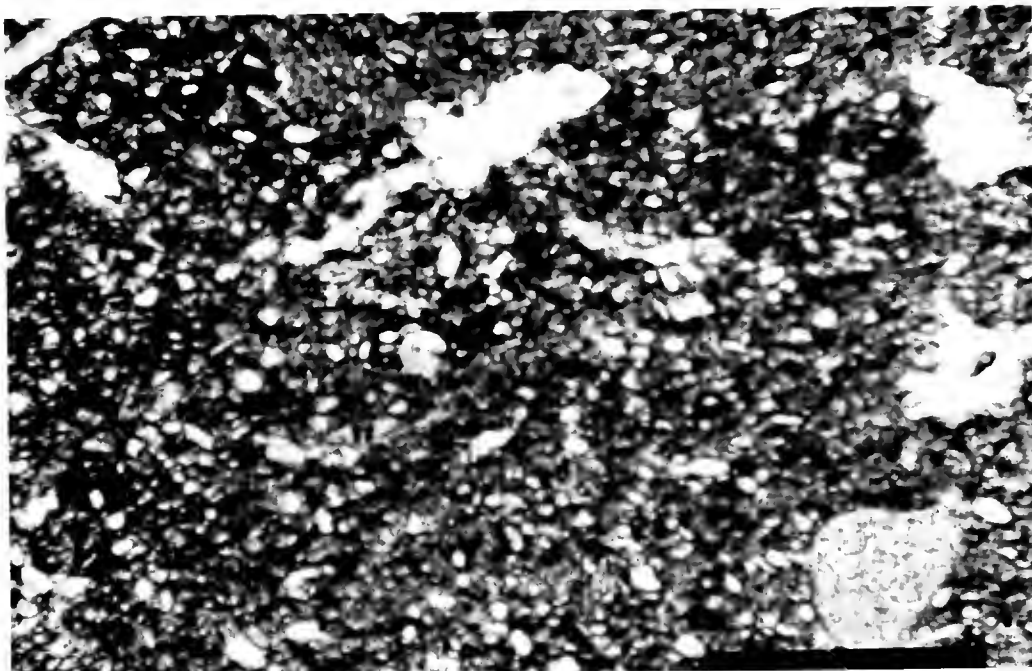


Figure 3: Photomicrograph of Earthenware Tile Thin Section in Transmitted Light (Magnification 100x).

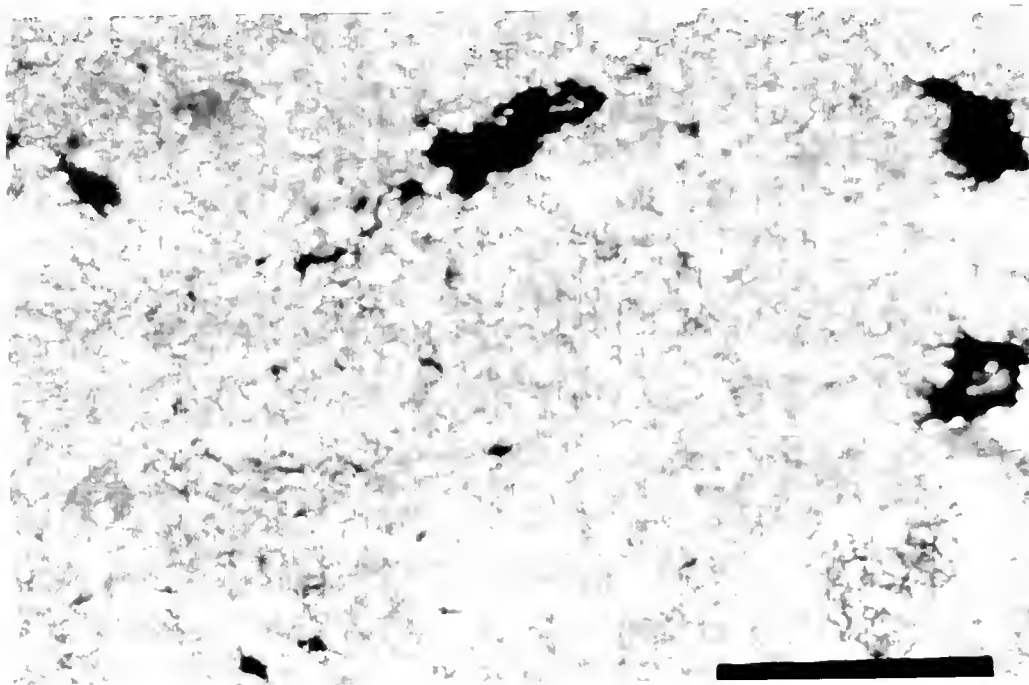


Figure 4: Photomicrograph of Earthenware Tile Thin Section in Crossed Polarized Light (Magnification 100x).

The grains were held together by a very fine grained red matrix composed of clays and the very fine quartz grains. Figures 1-4 show the general appearance of this material.

The yellow-pink stoneware tiles (Munsell 7.5YR Hue, 7 Value, 4 Chroma) were made by extruding a six by six centimeter clay slab of stoneware clay. They were fired at 1230 °C (cone 06). After firing, the average dimensions of the tiles were 5.3 centimeters by 5.4 centimeters by 1.4 centimeters, and the average weight of the stoneware tiles was 76.90 grams. These tiles were hard, and salt crystallization caused little damage.

The open porosity of the stoneware tiles was also determined by twenty-four hour immersion (ASTM C67-97) and five hour immersion in boiling water (ASTM C67-97). The results are given in Table 3. The open porosity of the stoneware tiles was significantly lower than that of the earthenware tiles. Further, a greater weight increase occurred during the boiling immersion experiment than did in the earthenware tiles, indicating a greater amount of very small pores.

Table 3: Porosity of Stoneware Tiles

| Tile | Porosity | Boiling |
|---------|----------|---------|
| A | 5.3% | 8.2% |
| B | 4.6% | 7.5% |
| C | 5.3% | 7.8% |
| D | 5.0% | 7.6% |
| Average | 5.1% | 7.8% |

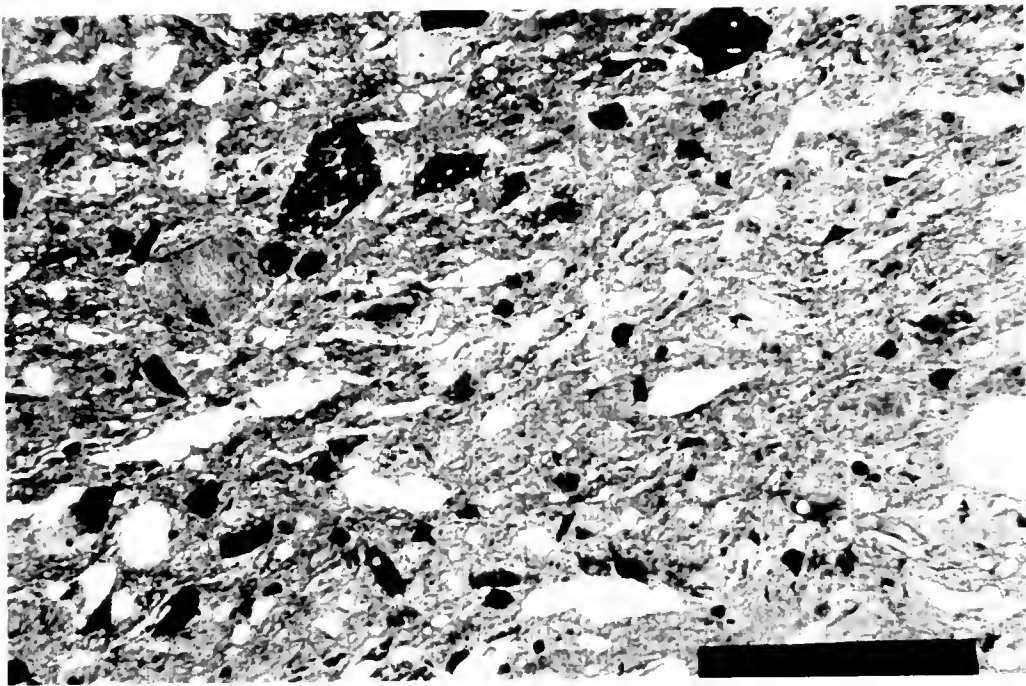


Figure 5: Photomicrograph of Stoneware Tile Thin Section in Transmitted Light (Magnification 25x).

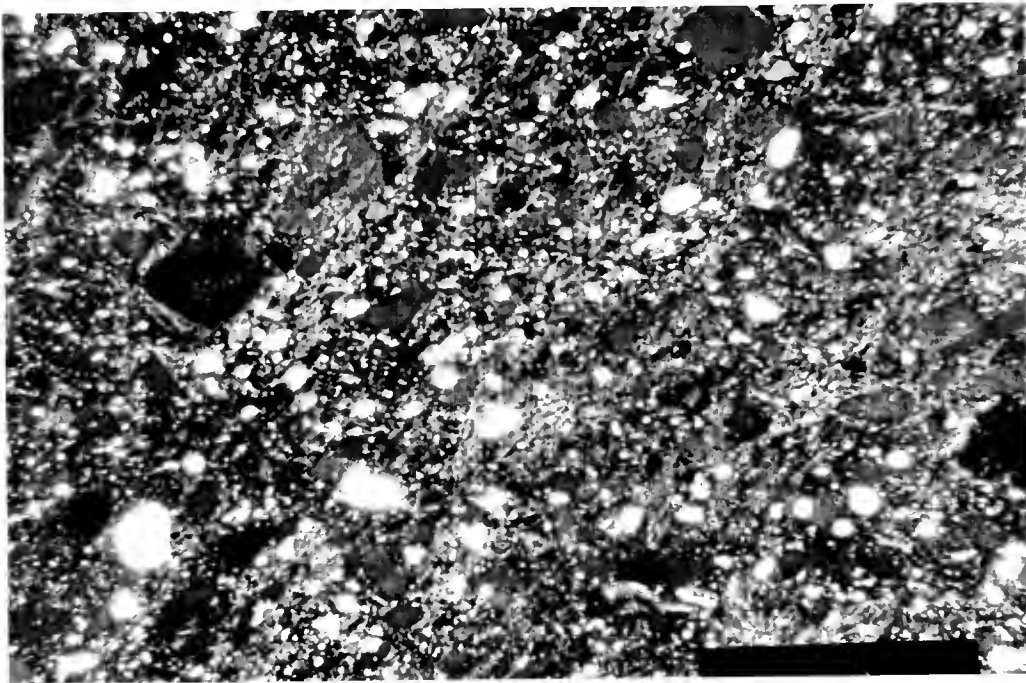


Figure 6: Photomicrograph of Stoneware Tile Thin Section under Cross Polarized Light.



Figure 7: Photomicrograph of Stoneware Tile Thin Section under Transmitted Light (Magnification 100x).

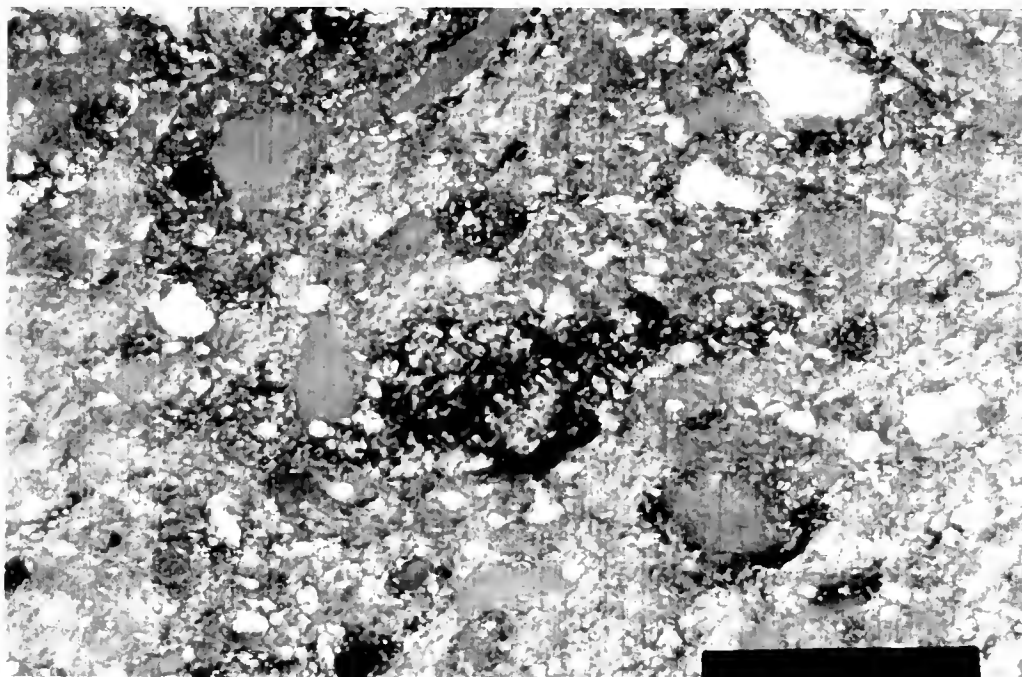


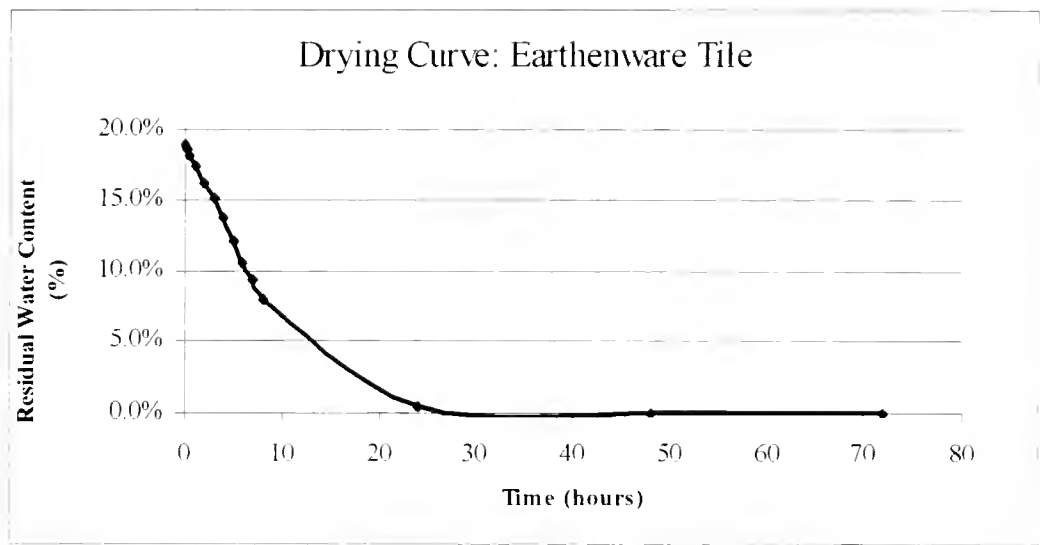
Figure 8: Photomicrograph of Stoneware Tile Thin Section under Cross Polarized Light (Magnification 100x).

Pore characterization was carried out with microscopic analysis of thin sections (Figures 5-8). The measurements are provided in Appendix C. While the stoneware tiles had a much lower porosity, most of the pore area was a result of a small number of large pores. Unlike the earthenware tiles; however, there were few medium sized pores. The long and narrow pore shape in the stoneware is a result of the extrusion manufacturing process.

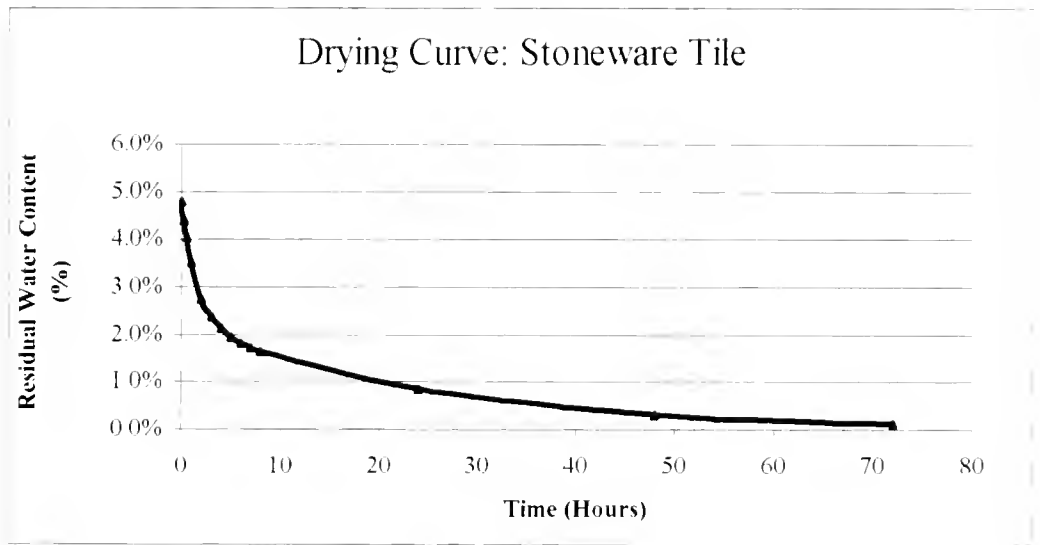
Polarized light microscopy was also used for mineralogical characterization of the stoneware tiles. As in the case of the earthenware tiles, silicate minerals predominated. The stoneware tiles had fewer but larger quartz grains than did the earthenware tiles. The quartz grains were well sifted with an average major and minor axis of 8.8×10^{-4} millimeters. Quartz comprised approximately 10% of the total area. The rest of the stoneware tiles was a fine grained gray clay matrix under transmitted light and brown-gray under cross polarized light. The clay also formed larger colloidal aggregates with small quartz grains within them. The clay was powdered and the refractive index was determined to be 1.56 using a collection of refractive index oils. Based on these observations, and the low first order interference color, the clay was determined to be kaolinite, a clay often used in the manufacture of tiles.

The drying rate of both tiles was determined according to NORMAL 29/88 and plotted in Graphs 1 and 2. The results confirm the observation of pore size determined by optical microscopy. The initial drying rate of the stoneware tiles was faster than the earthenware tiles because of the larger pores. The complete drying, however, took longer because of the finer pores evident in the boiling porosity test

Graph 1: Drying Rate of Earthenware Tile



Graph 2: Drying Rate of Stoneware Tiles



The earthenware had a consistent drying rate because of the interconnectedness of the pores, as indicated by the porosity measurements.

While both tiles had similar mineralogical compositions, their properties most notably open porosity and pore sizes were notably different. These characteristics had a tremendous effect on the desalination efficiency of the tiles.

5. ANALYTICAL TECHNIQUES

Conductance measurements and conductimetric titrations were chosen to quantitatively evaluate the amount of salts removed from the sets of tiles. Both of these techniques have the advantage of using simple and inexpensive instrumentation. Easy to interpret, the results can be extremely accurate. Both methods rest on the measurement of conductivity.

Conductivity is the ability of a solution to carry electricity due to the mobility of ions when subjected to an electric field. Most simply, conductance is the inverse of resistance. Conductance of a solution depends on the concentration of ions, and the specific ion's mobility, size, and valence. Conductance measurements are most suited for strong electrolytes because of the complete dissociation of the molecules. Sodium chloride, sodium sulfate, and gypsum are all strong electrolytes. Table 4 gives the equivalent conductance for the ions in question.

Table 4: Equivalent Ion Conductance at 25° C⁶⁰

| Ion | λ |
|----------------------------------|-----------|
| Na ⁺ | 50.1 |
| Cl ⁻ | 76.3 |
| Ag ⁺ | 61.9 |
| NO ₃ ⁻ | 71.4 |
| Na ⁺ | 50.1 |
| 1/2SO ₄ ²⁻ | 79.8 |
| 1/2Ca ²⁺ | 59.5 |
| 1/2Ba ²⁺ | 63.6 |

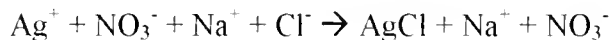
⁶⁰ Donald T. Sawyer, William R. Heineman, and Janice M. Beebe, *Chemistry Experiments for Instrumental Methods* (New York: John Wiley & Sons, 1984), p.59.

5.1 TITRATIONS

Titration involves the addition of a solution of known concentration, the titrant, to a solution of unknown concentration, the titrand. When an equivalent number of moles of titrant to the titrand have been added the endpoint has been reached marking the end of the reaction. This may be monitored using a colored indicator, or measuring changes in pH or conductance. A conductimetric titration specifically uses conductance to identify the endpoint. Since conductance readings are very sensitive, it is an ideal technique to mark the endpoint of a titration. Further, unlike using pH, the titration endpoint is calculated based on a number of readings, not requiring the measurement of the actual endpoint. This use of multiple readings reduces the difference between the equivalence endpoint and the visible endpoint that sometimes exist. As a result, the data is more accurate and less subject to technical or operator error than other titration techniques.

To evaluate the amount of salts present, two different titrants are used. First, silver nitrate is used to measure the concentration of chloride ions. Second, barium chloride is used to evaluate the concentration of sulfate ions.

Argentometric titrations utilize silver nitrate as the titrant because silver ions react rapidly with chloride ions. The reaction is:



The chloride ions precipitate with the silver ions, removing their contributing conductance and lowering the total conductance of the solution. Since the silver ion added also precipitates, it does not affect the conductance readings. The nitrate ion, however, remains in the solution and contributes to an increase in the total conductance.

Since the equivalent ionic conductance of the nitrate being added is slightly larger than the chloride ion being subtracted, the conductance of the solution increases minimally while the nitrate ion's contribution replaces the chloride ion's. Once all the chloride ions have completely reacted with the silver ions (the endpoint) the addition of more silver nitrate will increase the conductance of the solution more rapidly; since, both silver and nitrate ions will be adding conductance, and no ion is being removed from the solution.

Conductance varies greatly with concentration so that when the titrant is added the concentration of the solution decreases. This change in volume can be compensated for by multiplying the measured conductance against the correction factor $(V + v)/V$ where V equals the milliliters of initial volume, and v equals the milliliters of titrant added to the solution.⁶¹

Temperature also affects conductance by approximately 2.5% per degree Celsius.⁶² The best way to minimize this effect is to keep the solution in a hot oil bath which regulates the temperature within 0.01 °C. For the present experiments given the number of measurements taken, it was sufficient to keep the temperature constant to 1°C. This was achieved by a water bath at room temperature.⁶³

Given the linear relationship between conductance and concentration, when the results are plotted as conductance against milliliters of titrant added, the result will be two

⁶¹ F. W. Fifield and D. Kealey, *Principles and Practice of Analytical Chemistry 2nd Edition* (London: International Textbook Company Limited, 1983), p. 227; and Donald T. Sawyer, William R. Heineman, and Janice M. Beebe, *Chemistry Experiments for Instrumental Methods*, p. 63.

⁶² Donald T. Sawyer, William R. Heineman, and Janice M. Beebe, *Chemistry Experiments for Instrumental Methods*, p.63.

lines. The first line will have a slope of near zero. The slope of the second line will be positive. The endpoint will be determined by the intersection of these two lines. The points close to either side of the endpoint should be ignored when drawing the lines. In this region of the graph, curvature may occur as a result of the partial disassociation of the precipitates.⁶⁴ This curvature can be minimized by using the titrant at the strongest possible concentration.⁶⁵ After determining the endpoint, the number of equivalent moles of sodium chloride can be determined, and from it, the concentration or the weight of the salt in the solution can be calculated

Barium chloride is used to titrate either the sodium sulfate or the gypsum in these experiments. The two reactions are.



The result is very similar to the titration with silver nitrate. In both of the reactions, sulfate ions are removed from the solution, and chloride ions are added. There is no appreciable difference in conductance until there are no more sulfate ions present to react with the barium. At this point, conductance increases rapidly. Again, two lines are drawn once the points are plotted. The intersection of these two lines indicates the endpoint of the titration. The concentration of either of the sulfate salts can then be determined.

⁶³ Ralph N. Adams et al., *Treatise on Analytical Chemistry Part I Theory and Practice Volume 4 Section D-2 Electrical Methods of Analysis Chapter 42-5* (Easton, PA: John Wiley & Sons, 1963), p. 2579.

⁶⁴ F. W. Fifield and D. Kealey, *Principles and Practice of Analytical Chemistry 2nd Edition*, p. 218.

In order for an accurate precipitation titration to occur, the reaction must be fast and simple. Further, the resulting compound must be very insoluble. Table 5 lists the solubilities of the precipitates. Both silver chloride and barium sulfate are insoluble at room temperature.

Table 5: Solubility of Precipitates⁶⁶

| Salt | K_{sp} at 25°C | Grams per 100ml of water |
|-----------------|------------------------|--------------------------|
| Silver chloride | 1.56×10^{-10} | 0.000089 g (0°C) |
| Barium sulfate | 1.08×10^{-10} | 0.000246 g (25°C) |
| Silver sulfate | -- | 0.57 g (0°C) |

However silver sulfate is also fairly insoluble, so that the procedure was tested to determine whether this method would represent an error in solutions when both anions are present.

5.2 TEST TITRATIONS

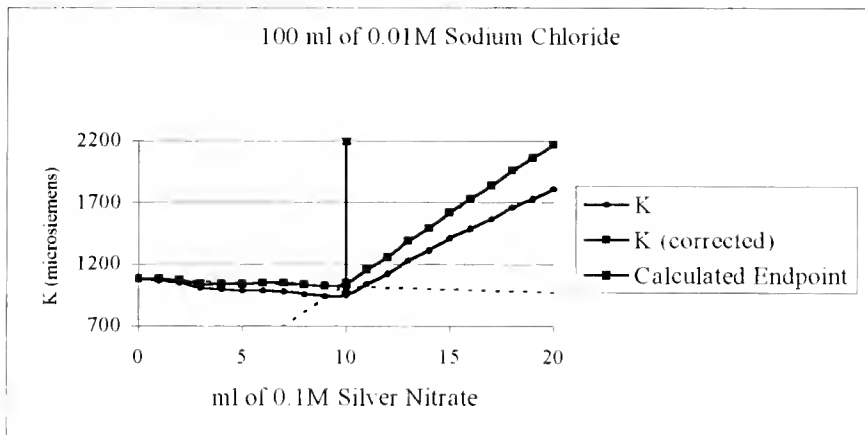
Test titration of a series of known standards were carried out before titration of unknowns to verify the accuracy of the technique and to quantify the potential error. In the first set of test titrations, the three salts sodium chloride, sodium sulfate, and gypsum were titrated in isolation (Table 6 and Graphs 3, 4, and 5).

⁶⁵ Ralph N. Adam et al. *Treatise on Analytical Chemistry: Part I Theory and Practice Volume 4 Section D-2 Electrical Methods of Analysis Chapter 42-5*, p. 2616.

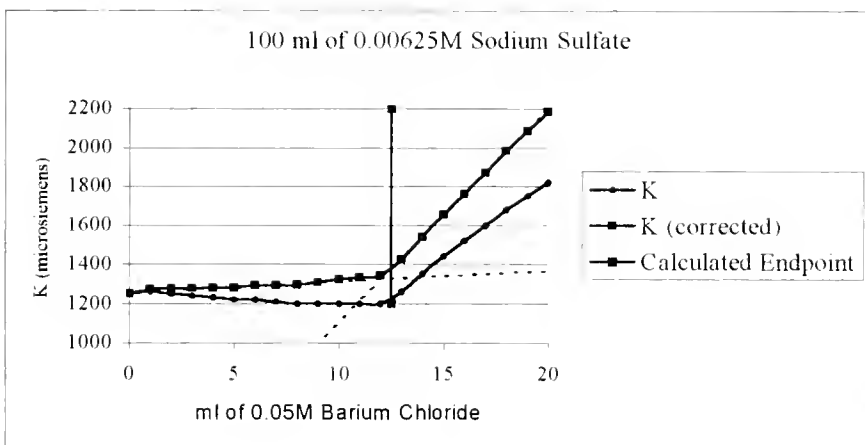
⁶⁶ Robert C. Weast (ed.). "Physical Constants of Inorganic Compounds." *CRC Handbook of Chemistry and Physics 58th Edition* (Cleveland: CRC Press. 1978). p. B-83-B178.

Test Titrations of Single Salts: Volume of Titrant vs. Conductance (K)

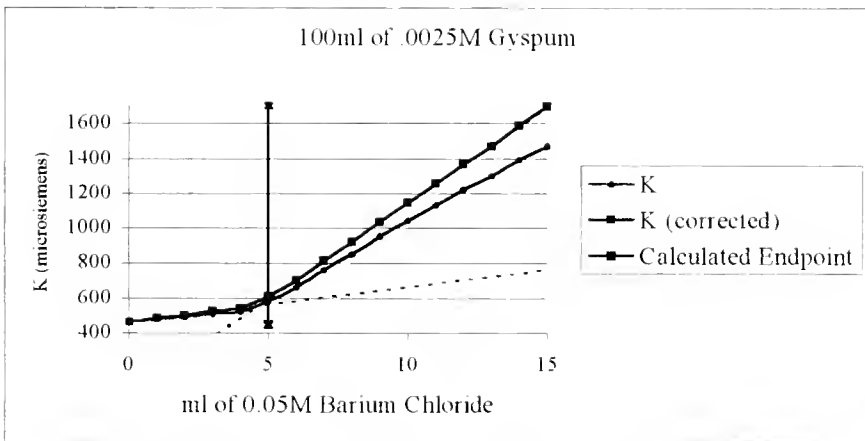
Graph 3: Chloride with Silver Nitrate



Graph 4: Sodium Sulfate with Barium Chloride



Graph 5: Gypsum with Barium Chloride



Solutions of 100 milliliters were prepared and titrated. The titration of the sodium chloride showed the highest degree of accuracy, accurate to 0.0001 grams per 100 milliliters (Graph 3). The titration of gypsum was the least accurate, accurate to 2 milligrams per 100 milliliters (Graph 5).

Table 6: Test Titrations of Single Salts

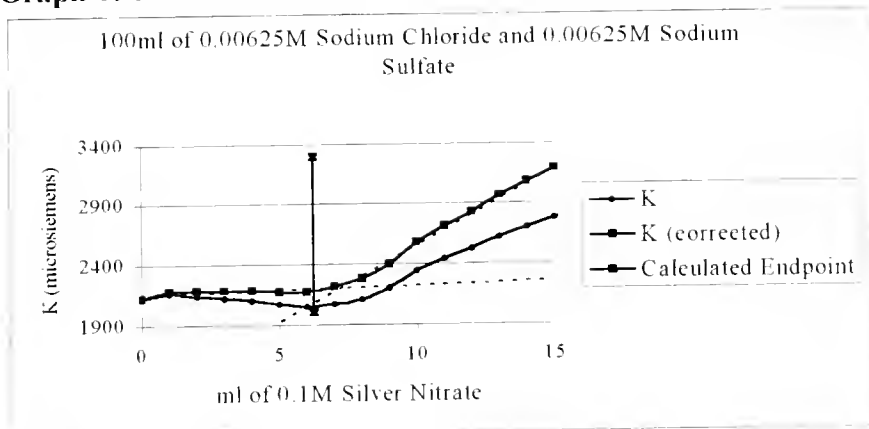
| Titration | Calculated Endpoint | Titration Endpoint | Molarity determined by Titration | Difference between calculated molarity and molarity determined by Titration | Difference in grams of salt between calculated grams and grams determined by titration |
|--|---------------------|--------------------|----------------------------------|---|--|
| 100ml of 0.01M NaCl with 0.1M AgNO ₃ | 10.0 ml | 9.84 ml | 0.0098 M | -0.002 M | -0.00012 g |
| 100ml of 0.00625M Na ₂ SO ₄ with 0.05BaCl ₂ | 12.5 ml | 12.0 ml | 0.006 M | -0.0025 M | -0.00036 g |
| 100ml of 0.0025M Gypsum with 0.05M BaCl ₂ | 5.0 ml | 4.7 ml | 0.0024 M | -0.0001 M | -0.0017 g |

All three titrations of the single salts had a reading just below the calculated salt concentration.

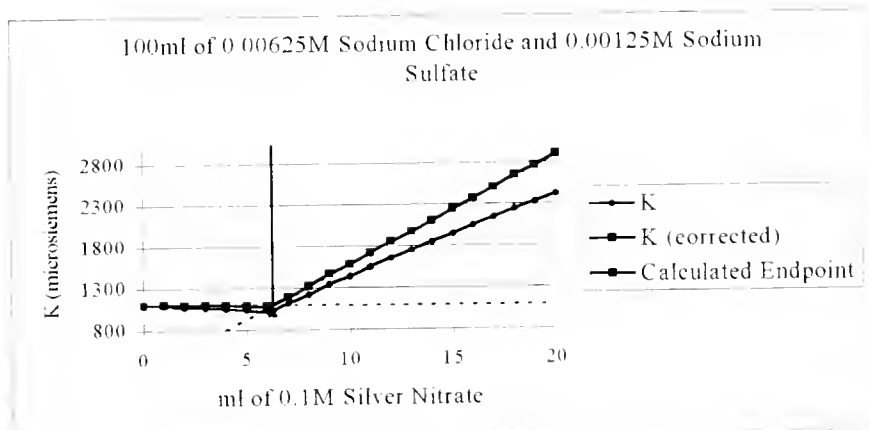
The next series of titrations were tested for sodium chloride content when mixed with sodium sulfate (Table 7 and Graphs 6, 7, and 8). Unlike the test of sodium chloride in isolation, each one of these tests slightly overestimated the sodium chloride concentrations.

Test Titrations of Sodium Chloride in the Presence of Sodium Sulfate: Volume of Silver Nitrate vs. Conductance (K)

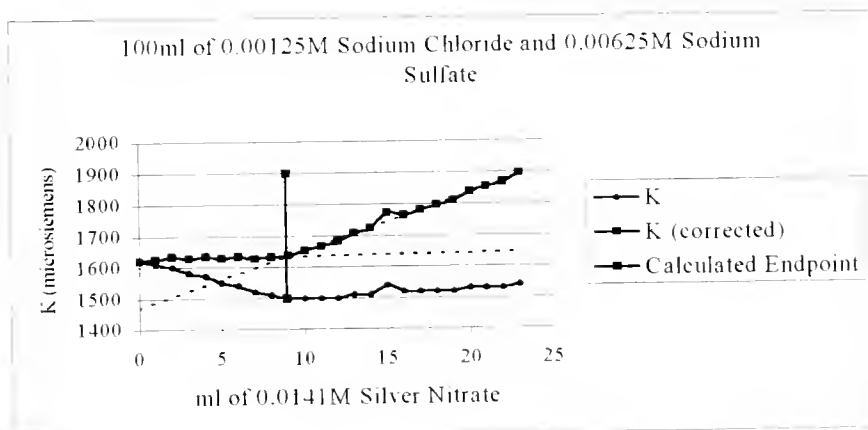
Graph 6: In the Presence of 0.00625M Sodium Sulfate



Graph 7: In the Presence of 0.00125M Sodium Sulfate



Graph 8: In the Presence of 0.00625M Sodium Sulfate



The test titration for sodium chloride in the most concentrated solution of sodium sulfate (0.00625 M) provided the least accurate results, 0.0056 grams above the calculated sodium chloride content (Table 7 and Graph 4). The endpoint of this graph is not as sharp as the single salt solution titrations. The curvature at the endpoint is a result of a small amount of silver ions reacting with the sulfate ions to form silver sulfate.

Table 7: Test Titrations of Sodium Chloride with Sodium Sulfate

| Titration | Calculated Endpoint | Titration Endpoint | Molarity determined by Titration | Difference between calculated molarity and molarity determined by Titration | Difference in grams of salt between calculated grams and grams determined by titration |
|--|---------------------|--------------------|----------------------------------|---|--|
| 100ml of 0.00625M NaCl and 0.00625 Na ₂ SO ₄ with 0.1M AgNO ₃ | 6.25 ml | 7.15 ml | 0.0072 M | 0.00095 M | 0.0056 g |
| 100ml of 0.00625M NaCl and 0.00125M Na ₂ SO ₄ with 0.1M AgNO ₃ | 6.25 ml | 6.30 ml | 0.0063 M | 0.00005 M | 0.0003 g |
| 100ml of 0.00125M NaCl and 0.00625M Na ₂ SO ₄ with 0.0141M AgNO ₃ | 8.9 ml | 9.0 ml | 0.001 M | 0.00025 M | 0.0015 g |

This error was not considered significant; since, this condition was unlikely to occur in the desalination solutions. The quantity of sodium chloride was always higher than the quantity of sodium sulfate during desalination due to the higher solubility of sodium

chloride. Approximately 77% of the total salt content of those tiles containing both sodium chloride and sodium sulfate was sodium chloride. Graph 8 shows the successful titration of a solution containing smaller amounts of sodium chloride, 0.00125 M. To titrate this solution, a titrant of lower concentration was used, 0.0141 M silver nitrate. While the slope of the second half of the titration curve has a smaller slope than the slope in the graphs using 0.1 M silver nitrate, the results were still accurate. Because of the large quantity of sodium chloride in the tiles, it was not generally necessary to use such a dilute titrant.

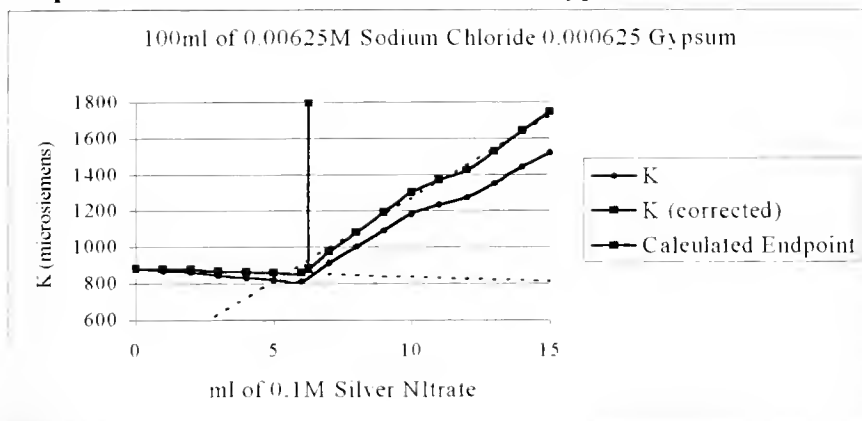
In the third set of test titrations, the sodium chloride content was tested for in the presence of gypsum (Table 8 and Graphs 9, 10, and 11).

Table 8: Test Titrations of Sodium Chloride with Gypsum

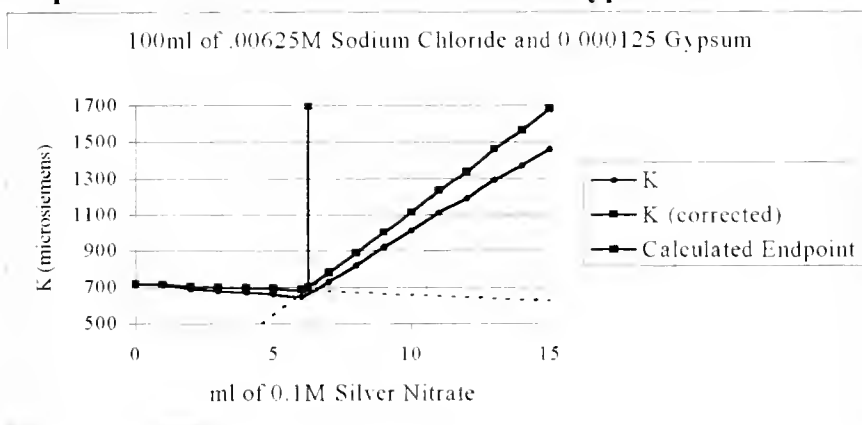
| Titration | Calculated Endpoint | Titration Endpoint | Molarity determined by Titration | Difference between calculated molarity and molarity determined by Titration | Difference in grams of salt between calculated grams and grams determined by titration |
|--|---------------------|--------------------|----------------------------------|---|--|
| 100ml of 0.00625M NaCl 0.000625 Gypsum with 0.1M AgNO ₃ | 6.25 ml | 5.46 ml | 0.0055 M | -0.007 M | -0.0044 g |
| 100ml of 0.00625M NaCl 0.000125 Gypsum with 0.1M AgNO ₃ | 6.25 ml | 6.2 ml | 0.0062 M | -0.00005 M | -0.00029 g |
| 100ml of 0.005M NaCl 0.0025 Gypsum with 0.1M AgNO ₃ | 5.0 ml | 4.8 ml | 0.0048 M | -0.0002 M | -0.0011 g |

Test Titrations of Sodium Chloride in the Presence of Gypsum: Volume of Silver Nitrate vs. Conductance (K)

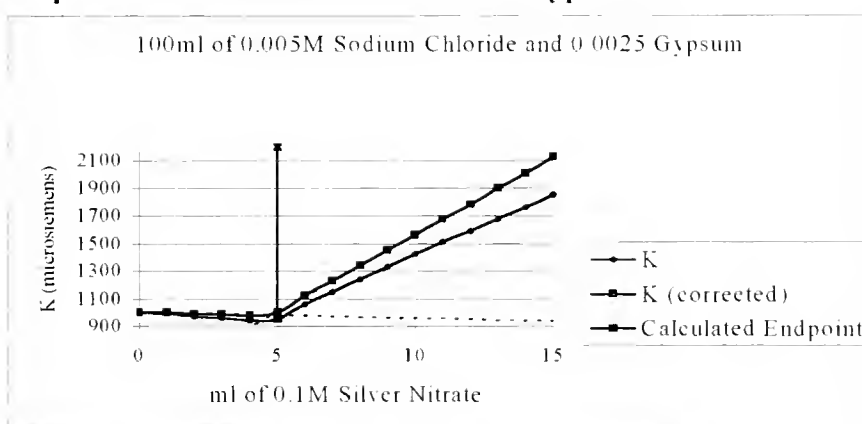
Graph 9: In the Presence of 0.000625M Gypsum



Graph 10: In the Presence of 0.000125M Gypsum



Graph 11: In the Presence of 0.0025M Gypsum

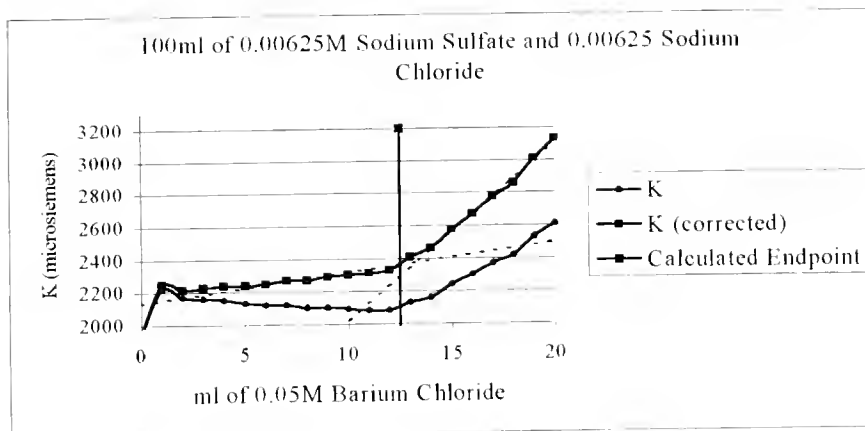


Since the solubility of gypsum is so much lower than that of sodium chloride, all of the solutions tested had a greater amount of sodium chloride than gypsum. All three titrations gave accurate results within a few milligrams. Like the single salt test titrations, the results understated the calculated content of sodium chloride. The gypsum did not have any effect on the titration of the sodium chloride.

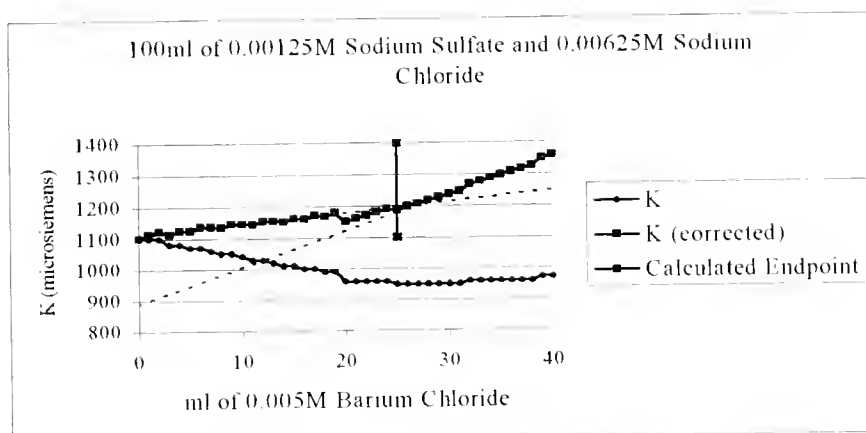
The fourth set of test titrations were used to verify the ability to determine the concentration of sodium sulfate in a sodium chloride solution (Table 9 and Graphs 12, 13, and 14). Again, the results show good accuracy. The difference between the calculated amount of grams and the titration amount of grams was within a few milligrams. All of these titrations gave a sodium sulfate concentration slightly higher than expected. Graph 13 illustrates the ability to determine the sodium sulfate content using a less concentrated titrant, 0.005M barium chloride. Just like the titrations using a titrant of a lower concentration of silver nitrate, the endpoint is less clear because the slope of the titration curve is smaller. In general, titrations for sodium sulfate when present with sodium chloride were not undertaken, since, estimating the concentration based on the conductance to molarity correlation curves gave accurate results.

Test Titrations of Sodium Sulfate in the Presence of Sodium Chloride: Volume of Titrant vs. Conductance (K)

Graph 12: In the Presence of 0.00625M Sodium Chloride



Graph 13: In the Presence of 0.00625M Sodium Chloride



Graph 14: In the Presence of 0.00125M Sodium Chloride

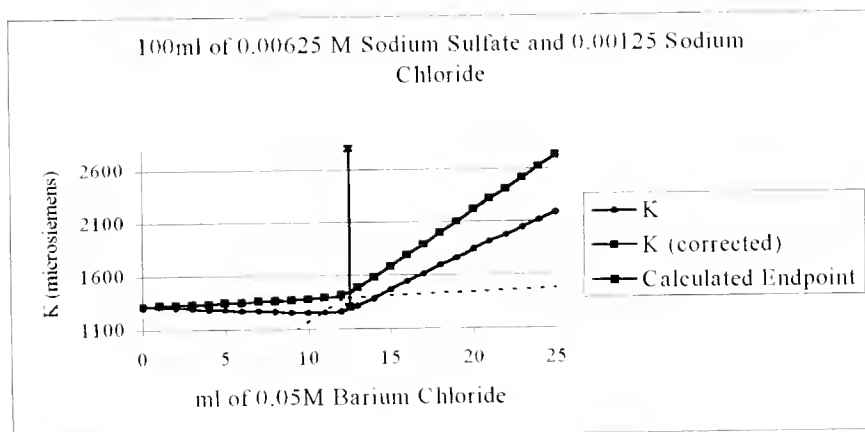


Table 9: Test Titrations of Sodium Sulfate with Sodium Chloride

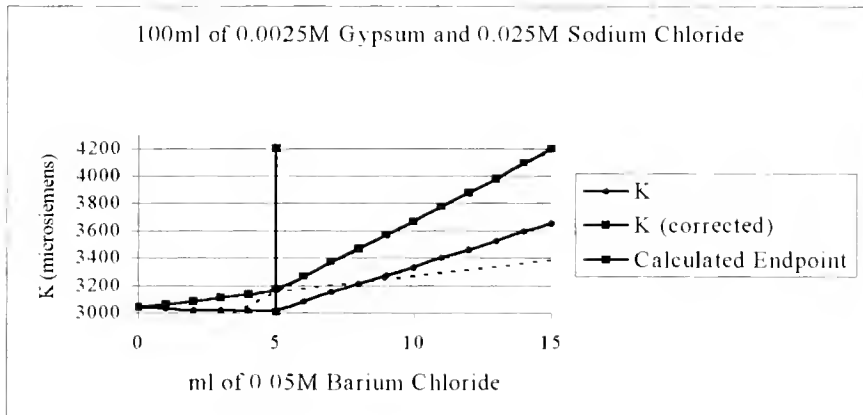
| Titration | Calculated Endpoint | Titration Endpoint | Molarity determined by Titration | Difference between calculated molarity and molarity determined by Titration | Difference in grams of salt between calculated grams and grams determined by titration |
|--|---------------------|--------------------|----------------------------------|---|--|
| 100ml of 0.00625M Na ₂ SO ₄ and 0.00625 NaCl with 0.05M Barium Chloride | 12.5 ml | 13.3 ml | 0.0067 M | 0.00045 M | 0.0064 g |
| 100ml of 0.00125M Na ₂ SO ₄ and 0.00625 NaCl with 0.005M Barium Chloride | 25 ml | 27 ml | 0.0014 M | 0.00015 M | 0.0021 g |
| 100ml of 0.00625M Na ₂ SO ₄ and 0.00125 NaCl with 0.05M Barium Chloride | 12.5 ml | 12.7 ml | 0.0064 M | 0.00015 M | 0.0021 g |

The final set of test titrations determined the concentration of gypsum within a sodium chloride solution (Table 10 and Graphs 15, 16, and 17). The results of Graphs 15 and 16 show the ability to determine the gypsum content when it is at least 0.0025 M.

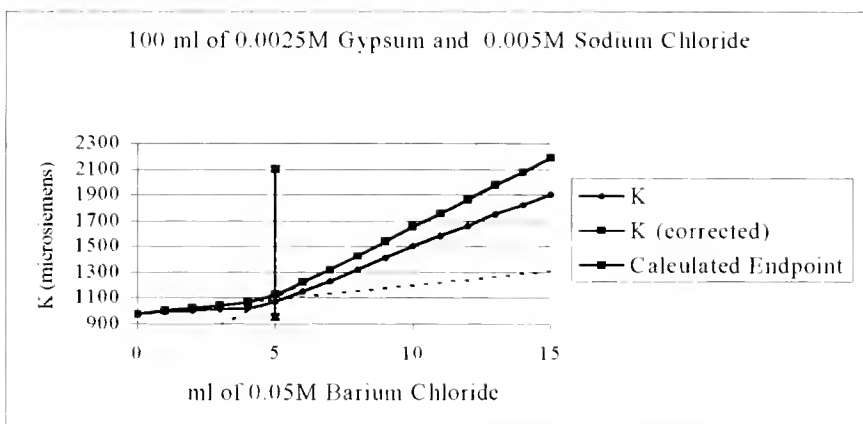
Graph 17 shows the results of a titration when the concentration of the titrand is too low. The two lines which are drawn do not intersect. The endpoint of the titration can not be determined; the conductance from the sodium chloride overwhelms any change due to the precipitation of barium sulfate.

Test Titrations of Gypsum in the Presence of Sodium Chloride: Volume of Titrant vs. Conductance (K)

Graph 15: In the Presence of 0.025M Sodium Chloride



Graph 16: In the Presence of 0.005M Sodium Chloride



Graph 17: In the Presence of 0.025M Sodium Chloride

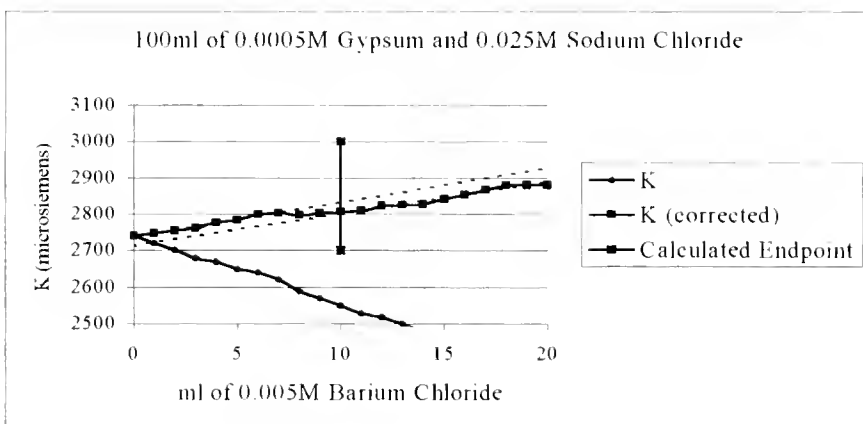


Table 10: Test Titrations of Gypsum with Sodium Chloride

| Titration | Calculated Endpoint | Titration Endpoint | Molarity determined by Titration | Difference between calculated molarity and molarity determined by Titration | Difference in grams of salt between calculated grams and grams determined by titration |
|--|---------------------|--------------------|----------------------------------|---|--|
| 100ml of 0.0025M Gypsum and 0.025M NaCl Titrated with 0.05M BaCl ₂ | 5.0 ml | 5.0 ml | 0.0025 M | 0.0 M | 0.0 g |
| 100ml of 0.0025M Gypsum and 0.005M NaCl Titrated with 0.05M BaCl ₂ | 5.0 ml | 4.8 ml | 0.0024 M | -0.0001 M | -0.0017 g |
| 100ml of 0.0005M Gypsum and 0.025M NaCl Titrated with 0.005M BaCl ₂ | 10 ml | No clear endpoint | No determination possible. | No determination possible. | No determination possible. |

The titration of gypsum within a sodium chloride solution was not generally necessary; since, an accurate quantification could be obtained from the molarity to conductance correlation curve.

These five sets of test titrations clearly show that an accurate quantification of both chloride and sulfate salts can be determined when the two types of salts are found together. The solutions tested were combinations that are beyond the range likely to occur during desalination, but even in these extreme cases accurate results were obtained.

5.3 CALIBRATION CURVES

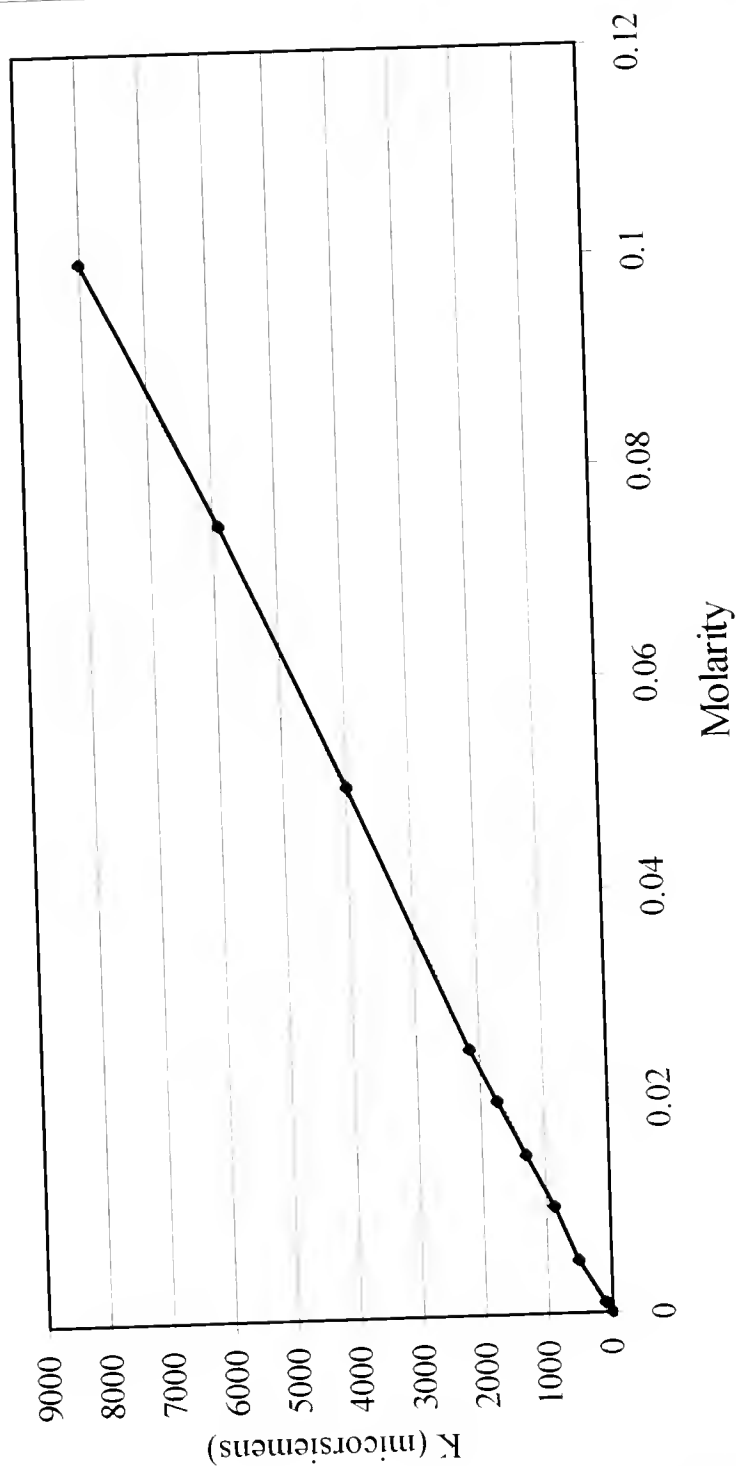
Conductance measurements were carried out on standard solutions at ambient lab conditions. The temperature ranged from 17 to 22 °C. The relative humidity ranged from 25% to 35% RH. With standard solutions of sodium chloride, sodium sulfate, and gypsum, calibration curves to correlate conductance to molarity were obtained. These curves were used to estimate the concentration of the salts. The sodium chloride solutions were prepared from a purchased standard 0.1 M solution. The sodium sulfate and gypsum solutions were prepared in the laboratory. All three conductance to molarity correlation curves illustrate the linear relationship between concentration and conductance (Graphs 18, 19, and 20).

5.4 TITRATION PROCEDURE

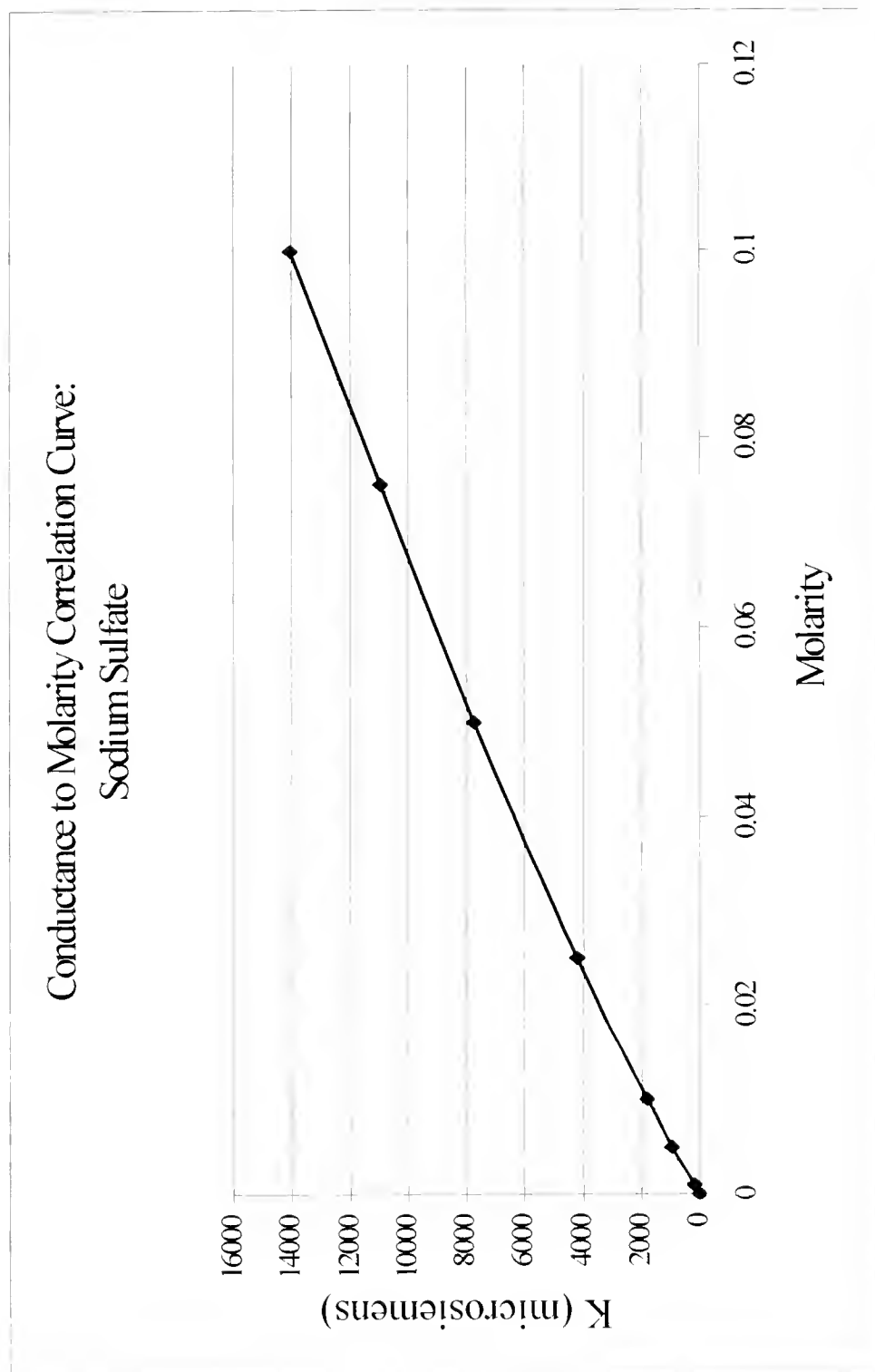
The test titrations indicated that a titration curve with a clear endpoint could be obtained by titrating one hundred milliliters of a 0.01 M solution of sodium chloride with a 0.1 M solution of silver nitrate. This concentration provided enough points before the endpoint to get the correct slope of the first conductance line. The endpoint would be at approximately ten milliliters. An accurate line could not be obtained using a solution with a concentration of less than a 0.00125 molar sodium chloride. By appropriately diluting an aliquot of the solution in which the tile was immersed, the titrand was prepared. For the earthenware tiles, it was occasionally necessary to dilute the solution twice.

Graph 18: Sodium Chloride Conductance (K) Standardization Curve

Conductance to Molarity Correlation Curve:
Sodium Chloride

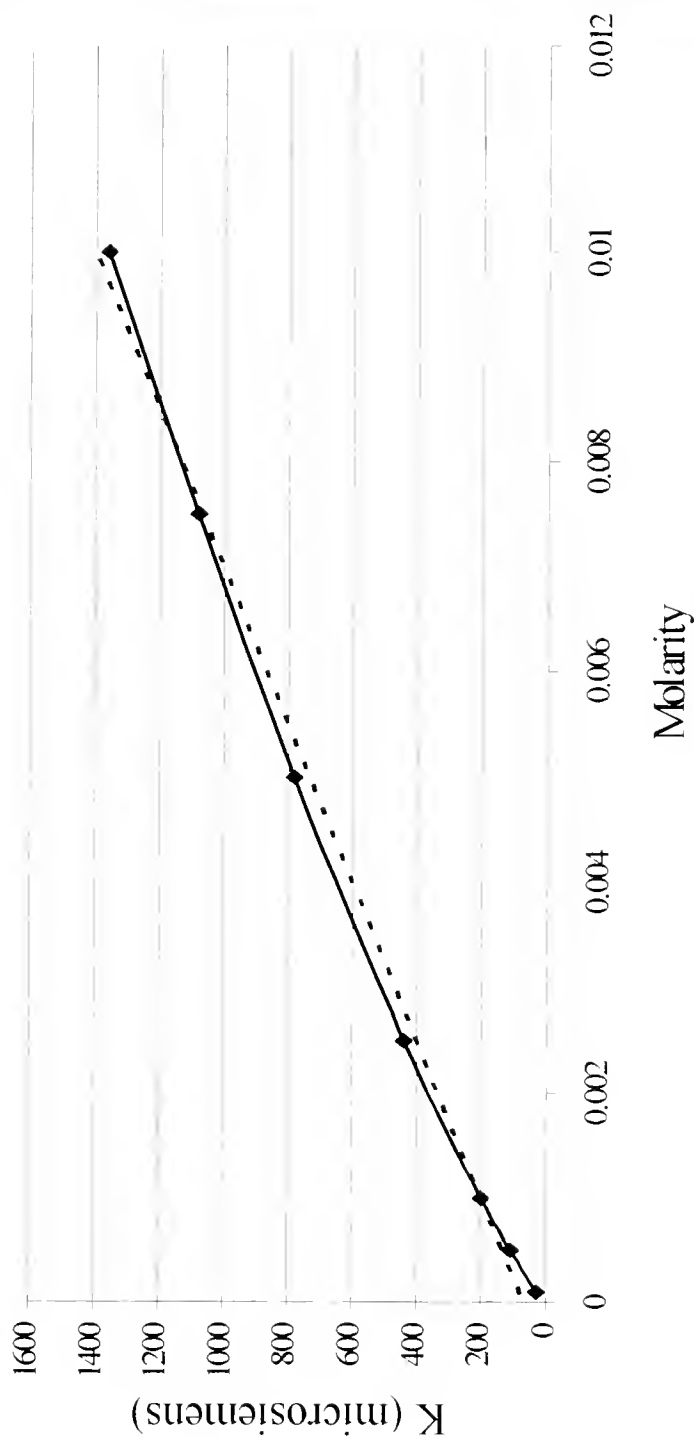


Graph 19: Sodium Sulfate Conductance (K) Standardization Curve



Graph 20: Gypsum Conductance (K) Standardization Curve

Conductance to Molarity Correlation Curve:
Calcium Sulfate Dihydrate



The test titrations for the sulfate salts indicated that one hundred milliliters of a 0.005 molar solution titrated with 0.05 molar barium chloride gave the most accurate results. This titrand was prepared and titrated.

For both titrations, a smaller volume of a more concentrated titrand could have been used, but the volume correction necessary for such titrations was far larger.

Once prepared, the solution was placed in a water bath, to regulate the temperature during the titration. A magnet was placed in the beaker with the solution, and the water bath and beaker were placed on top of the magnetic stirrer. The stirrer was set at a low speed. The calibrated conductance cell was placed in the solution and a reading was taken. The titrant was added one milliliter at a time from a twenty-five milliliter graduated burette. For titrating the chloride ions, fifteen to thirty seconds after each milliliter was added a conductance reading was taken. For the sulfate ion titrations the response was slower so the reading was taken after thirty to sixty seconds. After three equal successive measurements, the reaction was considered complete. The conductance value was recorded in microsiemens, and another milliliter of titrant was added.

The endpoint was immediately noticeable by the increase in the conductance reading. Another five to ten milliliters were added beyond the endpoint to have a suitable number of points to draw the titration curve.

The data from the titration was plotted with the conductance value along the y-axis and milliliters of titrant added along the x-axis. The actual conductance was multiplied by the volume correction value $(V + v)/V$ where V equals the initial volume

and v equals the number of milliliters added to the solution.⁶⁷ The resulting conductance values were plotted on the same graph as the uncorrected values. Using Microsoft Excel two trend lines were drawn omitting the values near the endpoint. The endpoint was determined by the intersection of the two trend lines. From the endpoint the molarity of the initial solution was determined. This molarity was translated to the total grams of salt in the solution.

When two salts were in combination, the procedure was as follows. First, the total conductivity of the solution was measured. Since, the concentration of the sodium chloride was far larger - nearly one order of magnitude greater than for sodium sulfate and almost two orders of magnitude greater than for gypsum - it contributed most of the conductance. The total conductance was used to estimate the molarity of sodium chloride so as to prepare the titrand. An aliquot of this solution was then diluted and titrated for chloride ions first. Using the conductance to molarity correlation curve for sodium chloride, the contributing conductance of the sodium chloride was determined. This contributing conductance was subtracted from the initial total conductivity measured. The sulfate salt was responsible for the remaining conductance. Using the subtracted conductance, the concentration of the sulfate salt was determined using the conductance to molarity calibration curve. If the concentration of the sulfate ion was large enough, the solution was titrated to confirm its concentration. Theoretically, relying on the conductance to molarity correlation curve, for the concentration of the sulfate salts in the

⁶⁷ F. W. Fifeild and D. Kealey, *Principles and Practice of Analytical Chemistry*, 2nd Edition, p. 227; and Donald T. Sawyer, William R. Heineman, and Janice M. Beebe, *Chemistry Experiments for Instrumental Methods*, p. 63.

presence of sodium chloride, underestimates the actual concentration because of interion interaction.⁶⁸ This difference is minimal in solutions of extremely low molarity. The accuracy of this technique was tested empirically. The results are shown in Table 11.

Table 11: Test Titrations of Conductance Estimated Concentrations

| Solution | Salt | Titration Molarity | Conductance Estimated Molarity | Titration Grams Removed in 150ml solution | Conductance Grams Removed 150ml Solution |
|---------------------|----------------|--------------------|--------------------------------|---|--|
| Tile E10 Solution 1 | Sodium Sulfate | 0.0185 M | 0.015 M | 0.39 g | 0.32 g |
| Tile E10 Solution 2 | Sodium Sulfate | 0.003 M | 0.0028 M | 0.064 g | 0.06 g |
| Tile E10 Solution 3 | Sodium Sulfate | 0.003 M | 0.003 M | 0.064 g | 0.0064 g |
| Tile E26 Solution 1 | Sodium Sulfate | 0.02 M | 0.018 M | 0.43 g | 0.38 g |
| Tile S45 Solution 2 | Gypsum | 0.0009 M | 0.0008 M | 0.02 g | 0.02 g |

⁶⁸ D. B. Hibbert and A. M. James, *Dictionary of Electrochemistry Second Edition*, (New York: John Wiley & Sons, 1984), p. 52.

6. DESALINATION TESTS

6.1 INTRODUCTION

Initial experimentation began by testing the tiles which only contained a single salt: sodium chloride, sodium sulfate, or gypsum. During this stage, the difference between salt removal from porous, friable, low-fired earthenware tiles and hard, less porous, high fired stoneware tiles was compared. Also, a comparison was made between the removal of the different salts in isolation. The results for the stoneware tiles impregnated with gypsum are not accurate given the combination of the low solubility of the salt and the low open porosity of the tile. Since the measurements were of the order of the experimental error, the results for these tests are not reported.

6.2 PROLONGED IMMERSION

The first method tested was simply the soaking of tiles in 150ml of deionized water. One hundred and fifty milliliters was chosen as the minimum amount of water necessary to cover a single tile placed in a 250ml beaker, the smallest beaker the tile could fit into. The tile sat on its edge resting against the side of the beaker to allow the water currents to disperse the salts. The tile was placed into a previously filled beaker. The beaker was covered and conductance measurements were taken every hour for the first eight hours and daily afterwards. Some texts suggest climatizing the tile in a environment with a relative humidity of 100% before immersion into the water, to

eliminate trapped air within the tile,⁶⁹ but the similarity in the porosity of the tiles with total immersion and boiling (Tables 2 and 3) indicated this extra step was not required; since, water at room temperature infiltrated most open pores.

In the case of the earthenware tile containing sodium chloride, after two and a half hours the conductance of the solution went beyond the range of the conductance meter used (19,990 microsiemens). In order to continue to monitor the salt removal, the solution was changed at that time. When the increase of conductance of two successive readings within twenty-four hours was minimal the soaking cycle was ended. The earthenware tiles remained in the 150ml of water for ten days. The stoneware tiles remained in the solution for eight days.

Table 12: Percent of Salts by Prolonged Immersion in 150 milliliters of Water

| Tile | Salt | Percent of Total Salts Removed |
|-------------|---------------------------------|---------------------------------------|
| E-18 | NaCl | 96.2% |
| E-64 | Na ₂ SO ₄ | 85.6% |
| E-40 | Gypsum | 70.8% |
| S-17 | NaCl | 86.9% |
| S-66 | Na ₂ SO ₄ | 76.0% |

The results clearly show two trends (Table 12). First, all salts were more easily removed from the earthenware tiles than from the stoneware tiles. This relates to the difference between the total porosity and pore size distribution of the two sets of tiles.

⁶⁹ Colin Pearson (ed.), *Conservation of Marine Archaeological Objects*. (London: Buttersworth, 1987). p.

Second, the sodium chloride is easiest to remove followed by the sodium sulfate. The removal of the gypsum was the most difficult. This difference is a result of the difference in the solubility of the salts.

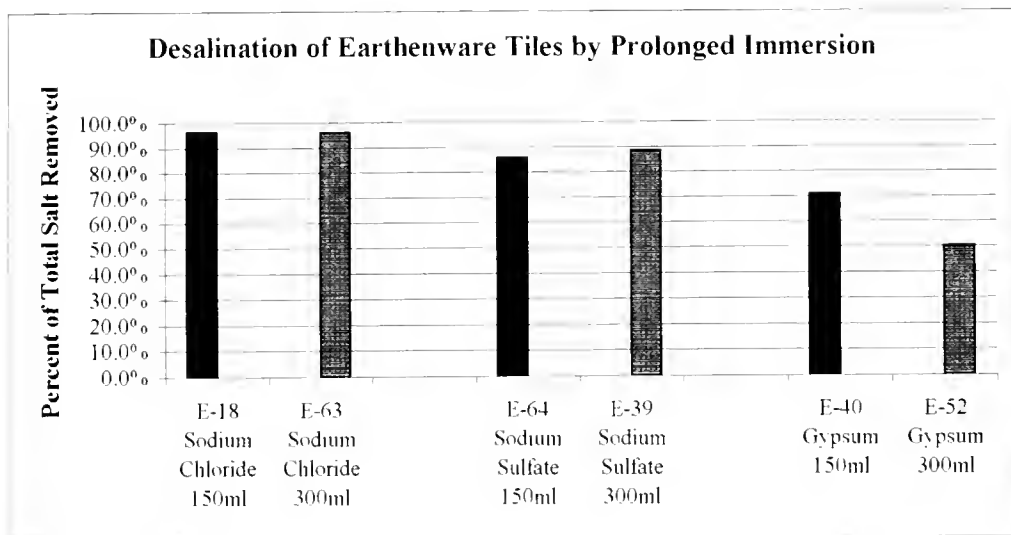
Many sources suggest that a large amount of water is needed to effectively desalinate objects. A typical suggestion is that 10 milliliters of water is needed for every 1 gram of object to be washed.⁷⁰ To test the hypothesis that a large amount of water is necessary to desalinate salts from ceramics, the first experiment was repeated using 300 milliliters instead of 150 milliliters of deionized water (Table 13). The tiles were set on glass beads to allow for the circulation of the solutions. Tiles were chosen with the closest amount of total salts as their counterparts had in the first Experiment. Again, for the earthenware tile treated with sodium chloride, tile E63, the solution was changed after seventy-two hours because the conductance of the solution surpassed the range of the conductance meter.

The results, summarized in Graphs 21 and 22, disproved the hypothesis that a large volume of wash solution is necessary. There was no significant difference between these two tests. The amount of water used does not significantly alter the efficiency of desalination. The results show the same correlation as the first experiment, the removal of salts as a function of tile porosity and salt solubility.

257.

⁷⁰ J Ciabach and Slawomir Skibinski, "Analyses of the Total Salt Content and Control of Salt Removal from Stone Historical Objects," in *The Conservation of Monuments in the Mediterranean Basin The Influence of Coastal Environment and Salt Spray on Limestone and Marble Proceedings of the 1st International Symposium Bari 7-10 June 1989*, ed. Fulvio Zezza (Brescia, Italy: Grafo, 1990), p. 325-328.

Graph 21: Comparison of Desalination by Prolonged Immersion



Graph 22: Comparison of Desalination by Prolonged Immersion

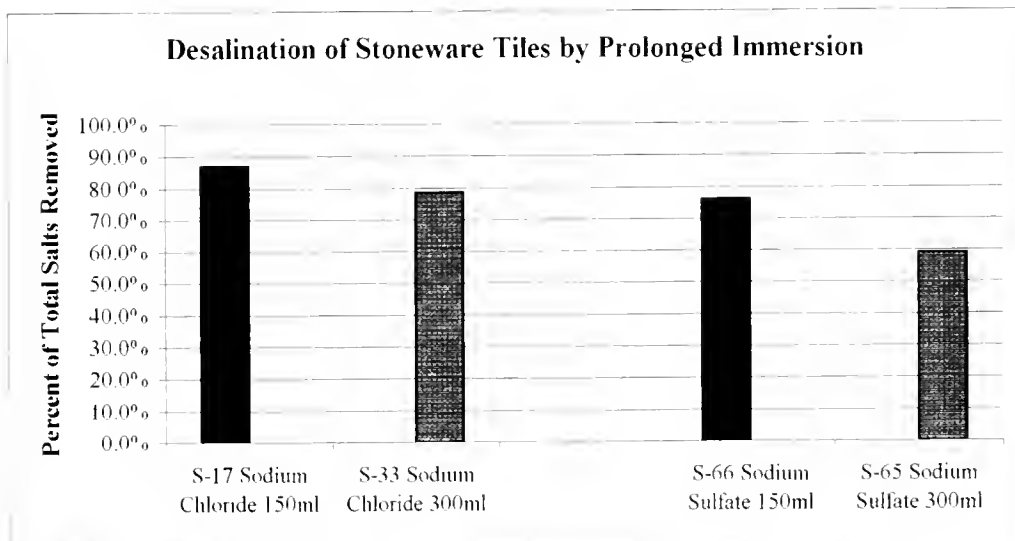


Table 13: Percent of Salts by Prolonged Immersion in 300 milliliters of water

| Tile | Salt | Percent of Total Salts Removed |
|-------------|---------------------------------|---------------------------------------|
| E-63 | NaCl | 96.0% |
| E-39 | Na ₂ SO ₄ | 88.3% |
| E-52 | Gypsum | 50.0% |
| S-16 | NaCl | 78.6% |
| S-65 | Na ₂ SO ₄ | 59.1% |

6.3 REPEATED WASHINGS

To increase the wash efficiency, the immersion solution was changed after short intervals. The first two experiments with tiles containing sodium chloride show the rate of desalination declines after the first hour (Appendix D Graphs D1-D4). For the tiles containing sodium chloride, 150 milliliters solution was changed every hour five times. The results are reported in Table 14.

Table 14: Percent of Salt Removed During Repeated Washings with 150 milliliters

| Tile | Salt | Percent of Total Salt Removed | | | | | |
|------|---------------------------------|-------------------------------|-------|-------|-------|-------|---------|
| | | Sol.1 | Sol 2 | Sol 3 | Sol 4 | Sol 5 | Total % |
| E-47 | NaCl | 49.7% | 4.5% | 3.2% | 2.6% | 2.4% | 62.4% |
| E-51 | Na ₂ SO ₄ | 26.3% | 5.6% | 4.4% | 4.4% | 4.4% | 45.1% |
| E-68 | Gypsum | 7.7% | 2.3% | 1.5% | 1.5% | 1.5% | 15.4% |
| S-46 | NaCl | 30.9% | 0.90% | 0.90% | 0.90% | 0.90% | 34.5% |
| S-50 | Na ₂ SO ₄ | 16.7% | 1.7% | 1.7% | 1.7% | 1.7% | 20.0% |

For the case of tiles with sulfate salts, the rate decrease occurred after two hours (Appendix D Graphs D5-D10). For these tiles the water was changed every two hours. One hundred and fifty milliliters of water and a total of five solutions were used.

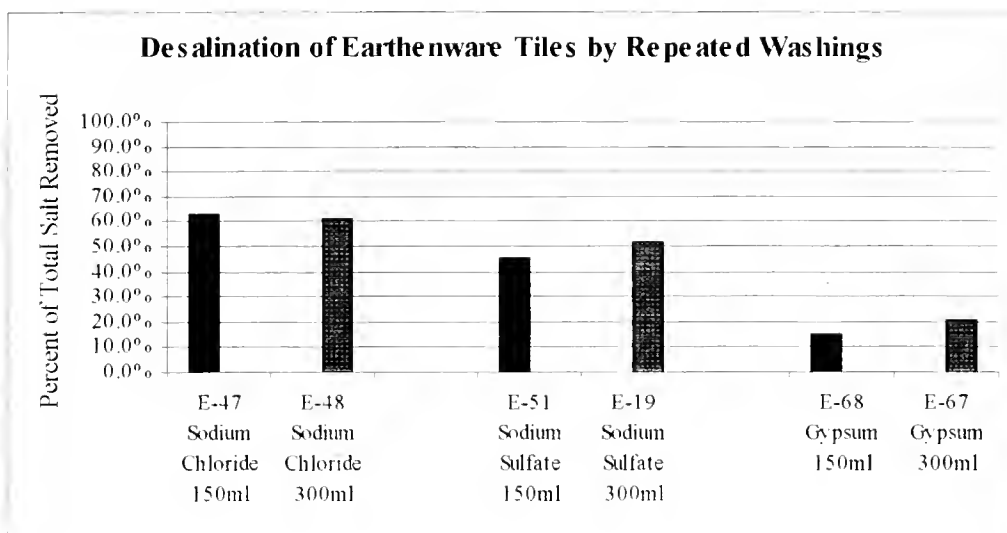
The experiment was repeated using a 300ml wash solution, to further verify that increasing the volume of the wash solution has no effect. The results are reported in Table 15. Again, no significant difference was observed between the 150 and 300 milliliter wash solutions, as shown in Graphs 23 and 24.

Table 15: Percent of Salt Removed During Repeated Washings with 300 milliliters

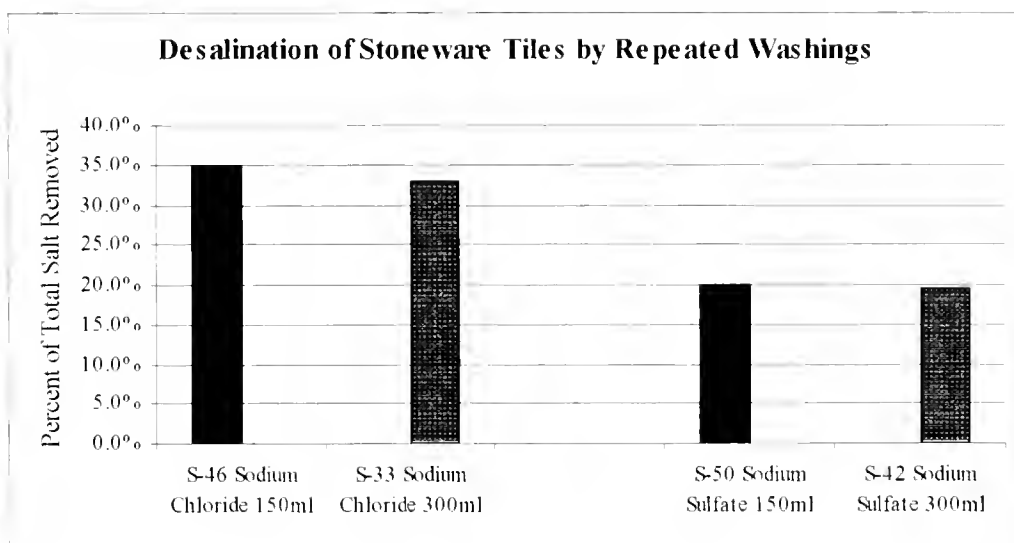
| Tile | Salt | Percent of Total Salt Removed | | | | | |
|------|---------------------------------|-------------------------------|-------|-------|-------|-------|---------|
| | | Sol.1 | Sol 2 | Sol 3 | Sol 4 | Sol 5 | Total % |
| E-48 | NaCl | 47.8% | 4.2% | 4.2% | 2.8% | 2.5% | 61.5% |
| E19 | Na ₂ SO ₄ | 33.1% | 6.0% | 4.8% | 4.0% | 4.0% | 51.9% |
| E-67 | Gypsum | 8.5% | 3.1% | 3.1% | 3.1% | 3.1% | 20.9% |
| S-33 | NaCl | 27.5% | 1.8% | 1.3% | 1.2% | 1.1% | 32.9% |
| S-42 | Na ₂ SO ₄ | 14.5% | 1.6% | 1.6% | 1.6% | 1.6% | 19.4% |

The total amount of salts removed remains less than that from the two tests using long term immersion. However, when comparing equal soaking times for both techniques, significantly more salt was removed by repeated washing. This is clearly shown in Graphs 25-29 presented in the next section. The removal of sodium chloride from the earthenware tiles was the most effective when compared to the sulfate salts. This is probably due to the higher mobility of the chloride ion. Again, the correlation between the solubility of the salt and the porosity of the tile remains.

Graph 23: Comparison of Desalination by Repeated Washings



Graph 24: Comparison of Desalination by Repeated Washings



The results confirm that the amount of wash solution has no affect on the efficiency of the desalination of the salts from the ceramic tiles.

To improve the washing efficiency, the tiles were allowed to partially dry between washings. This procedure was successfully applied to in situ washing by nebulization on buildings.⁷¹ The cycle included two steps: 1) washing the tiles in 150ml of deionized water; 2) allowing the tiles to air dry in between soakings. For the tiles treated with sodium chloride, each tile was left in solution for one hour. For the tiles treated with the sulfate salts, each tile was left in the solution for two hours. After the soaking cycle, both the tiles with sodium chloride and with sulfate salts were left to air dry for four hours. This timeframe was chosen because the stoneware tiles lost approximately half of the water weight gained in the immersion cycle during this time.

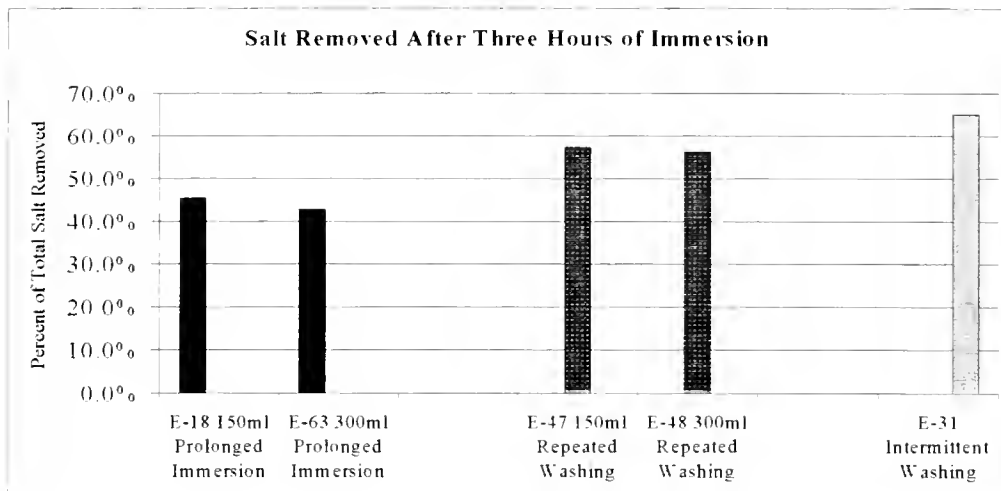
The results are presented in Table 16 and Graphs 25-29.

Table 16: Percent of Salt Removed During Intermittent Washings

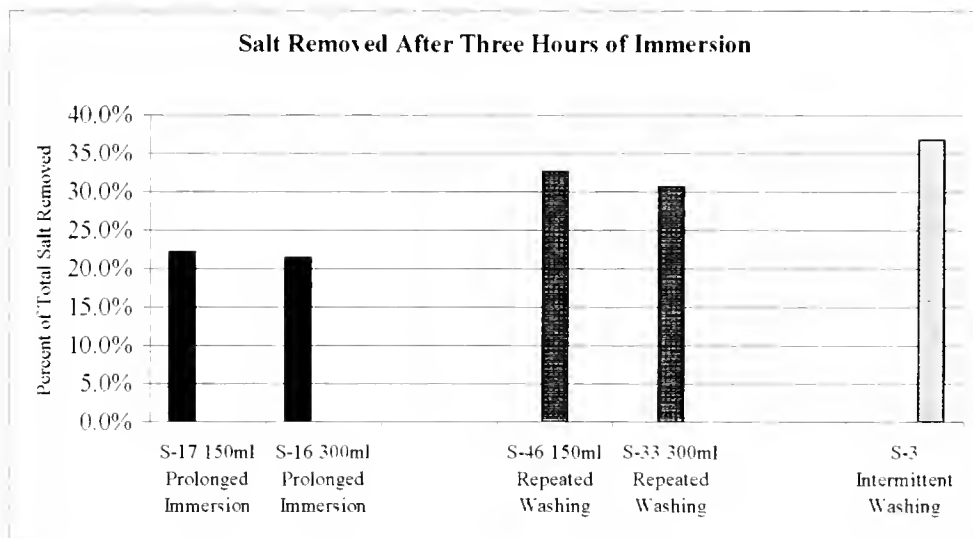
| Tile | Salt | Percent of Total Salt Removed | | | |
|------|---------------------------------|-------------------------------|-------|-------|---------|
| | | Sol.1 | Sol 2 | Sol 3 | Total % |
| E-31 | NaCl | 46.0% | 11.5% | 7.6% | 65.1% |
| E-6 | Na ₂ SO ₄ | 50.7% | 18.8% | 11.8% | 81.3% |
| E-22 | Gypsum | 25.0% | 25.0% | 20.0% | 70.0% |
| S-3 | NaCl | 23.7% | 5.3% | 7.9% | 36.9% |
| S-20 | Na ₂ SO ₄ | 12.3% | 3.8% | 5.1% | 21.8% |

⁷¹ G. Alessandrini, L.Toniolo, A. Antonioli, A. Di Silvestro, F. Piacenti, S. Righini Ponticelli and L. Formica. "On the Cleaning of Deteriorated Stone Materials," in *Conservation of Stone and Other Materials. Proceedings of the International RILEM UNESCO Congress, Paris, 1993*, ed. M.-J.Thiel. (London : E &FN Spon., 1993). p. 503-511.

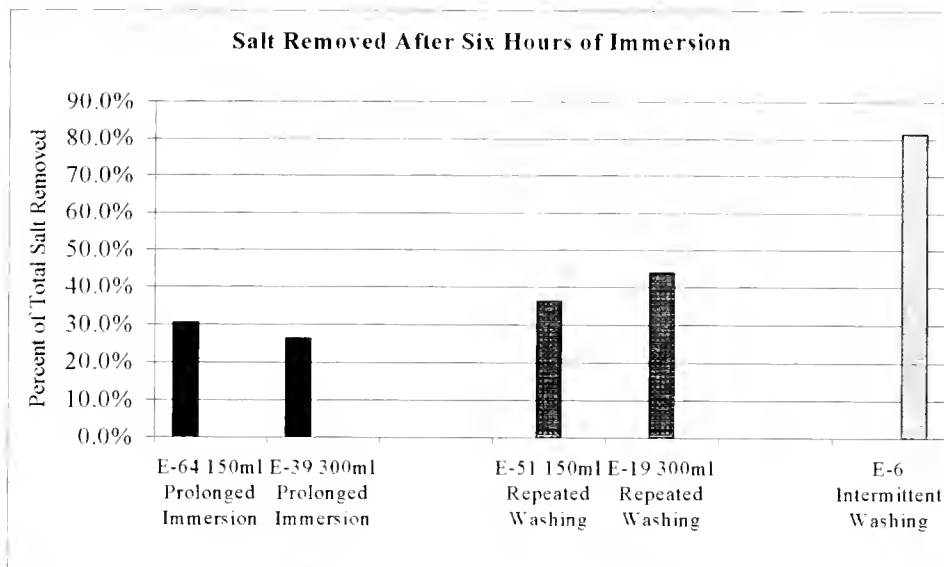
Graph 25: Comparison of Percent of Sodium Chloride Removed from Earthenware Tiles After 3 Hours in Water



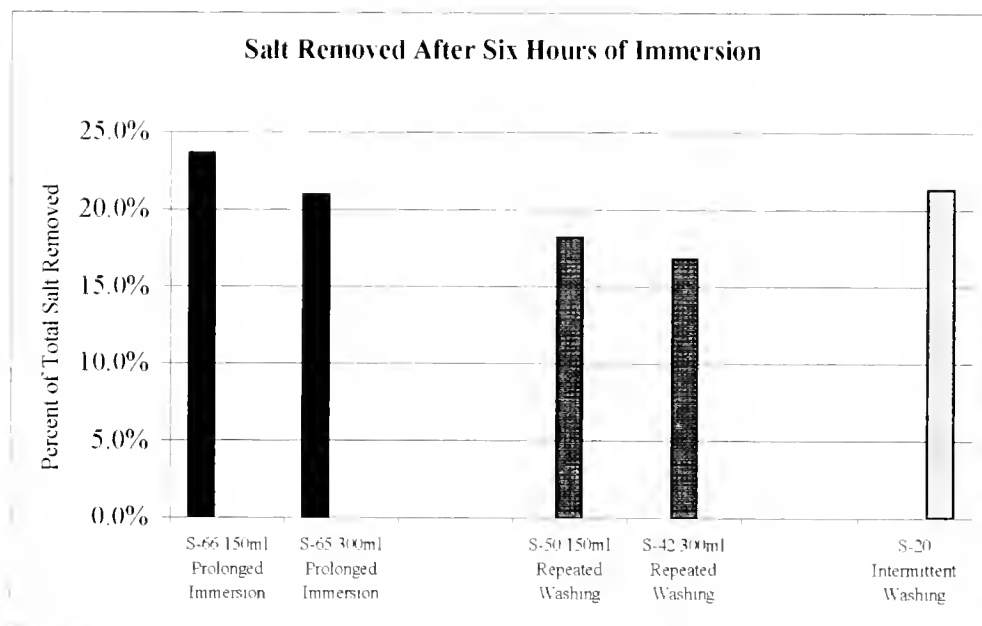
Graph 26: Comparison of Percent of Sodium Chloride Removed from Stoneware Tiles After 3 Hours in Water



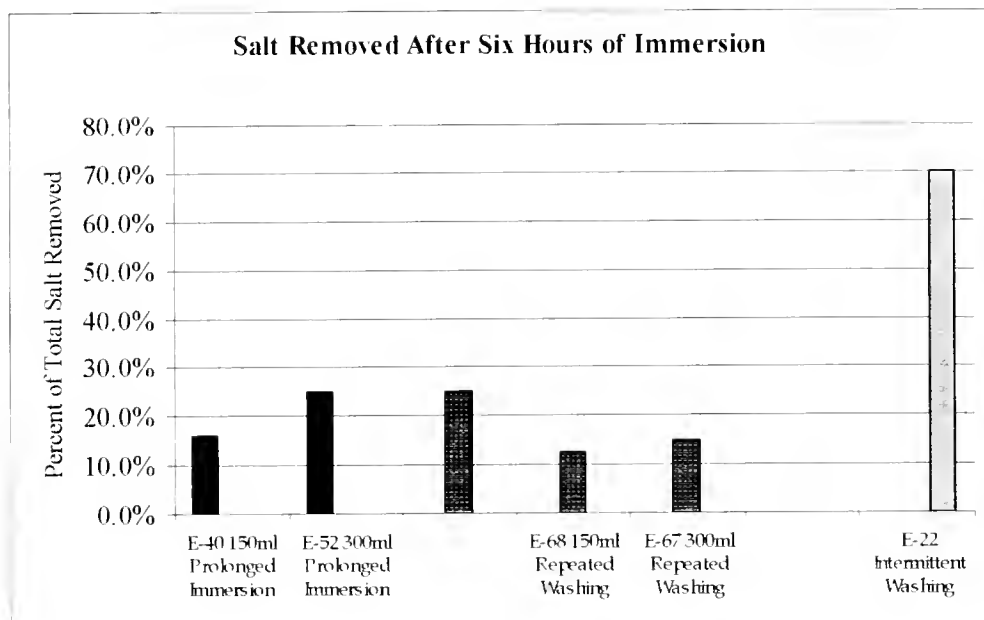
Graph 27: Comparison of Percent of Sodium Sulfate Removed from Earthenware Tiles After 6 Hours in Water



Graph 28: Comparison of Percent of Sodium Sulfate Removed from Stoneware Tiles After 6 Hours in Water



Graph 29: Comparison of Percent of Gypsum Removed from Earthenware Tiles After 6 Hours in Water



Even with only three cycles, the total amount of salt removed was equal or greater than the total amount of salt removed after five cycles of simple immersion for the same time. When compared to immersion after an equal amount of time, the differences are even larger (Graphs 25-29).

While this technique proves to be the most efficient, the sodium sulfate in the stoneware tile (S20) treated with sodium sulfate began to crystallize on the surface of the tile. When applying this technique in the field, care must be taken to shorten the amount of drying time to prevent this crystallization which will contribute to the deterioration of the object.

6.4 REMOVAL OF SALT MIXTURES

In order to evaluate the desalination of different salts when in combination, the tiles were desalinated by the intermittent washing technique. Both earthenware and stoneware tiles with sodium chloride and sodium sulfate or sodium chloride and gypsum were immersed for one hour in deionized water; since, the majority of the salt contained within the tiles was sodium chloride. Again, the tiles were allowed to air dry four hours in between each washing.

Table 17: Percent of Salt Removed During Intermittent Washings from Earthenware Tiles

| Tile | Salt | Percent of Salt Removed | | | |
|------|---|-------------------------|-------|-------|---------|
| | | Sol.1 | Sol 2 | Sol 3 | Total % |
| E-10 | NaCl Na ₂ SO ₄ | 34.4% | 7.0% | 6.5% | 47.9% |
| E-26 | NaCl Na ₂ SO ₄ | 37.5% | 7.3% | 7.0% | 51.8% |
| E-72 | NaCl Na ₂ SO ₄ | 40.3% | 6.2% | 5.2% | 51.7% |
| E-14 | NaCl Gypsum | 23.3% | 11.5% | 9.9% | 44.7% |
| E-30 | NaCl Gypsum | 18.6% | 7.2% | 7.2% | 33.0% |
| E-43 | NaCl Gypsum | 25.7% | 8.7% | 7.8% | 42.2% |

The results, presented in Tables 17 and 18, again show that desalination of tiles with a higher porosity was more efficient. For these, the average percent of the total salts removed was approximately 48% compared with approximately 23% for the stoneware tiles.

Table 18: Percent of Salt Removed During Intermittent Washings from Stoneware Tiles

| Tile | Salt | Percent of Salt Removed | | | |
|------|---|-------------------------|-------|-------|---------|
| | | Sol.1 | Sol 2 | Sol 3 | Total % |
| S-57 | NaCl Na ₂ SO ₄ | 12.5% | 3.7% | 4.4% | 20.6% |
| S-70 | NaCl Na ₂ SO ₄ | 11.3% | 3.2% | 3.8% | 18.3% |
| S-34 | NaCl Na ₂ SO ₄ | 12.5% | 2.9% | 2.9% | 18.4% |
| S-45 | NaCl Gypsum | 20.3% | 3.9% | 7.9% | 31.6% |
| S-29 | NaCl Gypsum | 16.7% | 4.2% | 2.8% | 23.6% |
| S-73 | NaCl Gypsum | 25.7% | 2.7% | 2.7% | 31.1% |

The amount of each individual salt in the tiles was calculated on the basis of the solubility graphs of the salts considered.⁷² It was assumed the same ratio of salts found in

⁷² Clifford Price and Peter Brimblecombe, "Preventing Salt Damage in Porous Materials," in *Preventive Conservation, Practice, Theory and Research: Preprints of the Contributions to the Ottawa Congress, 12-16 September 1994* (London: International Institute for Conservation of Historic and Artistic Works, 1994), p. 90-93; and Micahel Steiger and Anke Zennert, "Crystallization Properties of Salt Mixtures: Comparison of Experimental results and Model Calculations," in *Proceedings of the 8th*

the saturated solutions used for the impregnation remained in the tiles. It was found that the rate of removal was the same for sodium chloride as it was for the sulfate salts.

The equal rate of removal could be observed by comparing the ratio of the amount of sodium chloride to sodium sulfate salt removed with that in the tiles as calculated from the concentration at the eutonic point of the solubility graphs. The ratios are presented in Tables 19 and 20.

For the earthenware tiles, it can be seen that in the case of the tiles containing both sodium chloride and sodium sulfate the ratio remains essentially constant within experimental error, in particular by the third extraction. For the tiles containing sodium chloride and gypsum, the ratios are more erratic because the amount of gypsum measured is near the detection limit of the technique. The values, however, are within the same order of magnitude.

For the case of the stoneware tiles, only the data for the tiles containing sodium chloride and sodium sulfate will be reported (Table 20). Given the small amount of gypsum in these tiles the ratios could not be calculated.

Table 19: Ratio of Amounts of Sodium Chloride to Sulfate Salt Removed From Earthenware Tiles

| Tile | Ratio of Salts in the Tiles | Ratio of Salts Removed in First Wash | Ratio of Salts Removed in Second Wash | Ratio of Salts Removed in Third Wash |
|--|-----------------------------|--|---------------------------------------|--------------------------------------|
| E10 Sodium Chloride Sodium Sulfate | 3.4 | 3.0 | 3.3 | 3.0 |
| E26 Sodium Chloride Sodium Sulfate | 3.4 | 2.2 | 3.5 | 3.3 |
| E72 Sodium Chloride Sodium Sulfate | 3.4 | 5.2 | 5.0 | 3.0 |
| E43 Sodium Chloride Gypsum | 52.6 | 33.5 | 44.0 | 40.0 |
| E14 Sodium Chloride Gypsum | 49.6 | 58.0 | 28.0 | 62.5 |
| E30 Sodium Chloride Gypsum | 58.0 | Sulfate ion concentration below detection limit. | 85.0 | 20.0 |

For the tiles impregnated with sodium chloride and sodium sulfate, the first washing generally removes a relatively higher amount of sulfate ions, i.e. the chloride to sulfate ratio is smaller than the calculated original ratio. By the third washing, the ratio of sodium chloride was closer to the original ratio.

Table 20: Ratio of Sodium Chloride to Sulfate Salt Removed From Stoneware Tiles

| Tile | Ratio of Salts Remaining | Ration of Salts Removed in First Wash | Ratio of Salts Removed in Second Wash | Ratio of Salts Removed in Third Wash |
|--|--------------------------|---------------------------------------|---------------------------------------|--------------------------------------|
| S34 Sodium Chloride Sodium Sulfate | 3.4 | 1.8 | 3.0 | 3.0 |
| S57 Sodium Chloride Sodium Sulfate | 3.4 | 2.4 | 4.0 | 5.0 |
| S70 Sodium Chloride Sodium Sulfate | 3.4 | 2.2 | 8.0 | 12.5 |

6.5 POULTICE

Aside from total immersion, the most common desalination technique is poulticing. Two different absorbent clays, attapulgite and bentonite were chosen for testing based on their reported high efficiency.⁷³ The tiles used had already been desalinated by the repeated washing technique. The clay was mixed with washed sand in a ratio of one part clay to two parts sand. This mixture limited the cracking of the poultice as it dried so that good contact between the poultice and the tile was maintained during drying. The mixture also improved the workability of the poultice. Deionized water was added to the mixture until suitable workability was achieved.

⁷³ Lorenzo Lazzarini and Gianni Lombardi. "Bentonite for Cleaning and Desalination of Stones," in *9th Triennial Meeting : Dresden, German Democratic Republic, 26-31 August, 1990 : Preprints*. (Los Angeles : ICOM Committee for Conservation, 1990), p. 336-342; and P. Andrew Lins. "Technical Notes," in *Dutch Tiles in the Philadelphia Museum of Art*, ed. Jan Daniel van Dam and Pieter Jan Tichelaar (Philadelphia: Philadelphia Museum of Art, 1984).

The tile surface was wetted with a spray of deionized water and placed on a impermeable surface. The poultice was applied to all exposed surfaces of the tile at least one centimeter thick. The tiles were allowed to air dry. After twenty-four hours, the poultice began to crack and detach from the tile. At this time, the poultice was removed from the tile. The poultice containing the salts was dried in an oven at 100 °C until a constant weight was obtained. The dried poultice was then soaked in 150 milliliters of water and left covered for three days. During this time, the solution was occasionally stirred to insure that all the salts went into the solution.

Table 21: Percent of Salt Removed with Poultice

| Tile | Salt | Previous Treatment | Poultice | Percent of Salts Removed by Poultice |
|------|---------------------------------|------------------------|-------------|--------------------------------------|
| E48 | NaCl | 300ml Repeated Washing | Attapulgate | 35.5% |
| E47 | NaCl | 150ml Repeated Washing | Bentonite | 25.4% |
| E19 | Na ₂ SO ₄ | 300ml Repeated Washing | Attapulgate | 16.7% |
| E51 | Na ₂ SO ₄ | 150ml Repeated Washing | Bentonite | 22.7% |
| S33 | NaCl | 300ml Repeated Washing | Attapulgate | 37.0% |
| S46 | NaCl | 150ml Repeated Washing | Bentonite | Experimental Error |
| S42 | Na ₂ SO ₄ | 300ml Repeated Washing | Attapulgate | 18.0% |
| S50 | Na ₂ SO ₄ | 150ml Repeated Washing | Bentonite | 44.0% |

The resultant solution was then titrated as previously described. The results in Table 21 show that both of the absorbent clays give adequate desalination results, and no significant difference can be found between the use of bentonite or attapulgite.

6.6 PRESSURE POULTICE

The final desalination technique tested the efficiency of removal by using hydrostatic pressure to flush the salts from a porous material. The tiles containing salt combinations and used during the intermittent washings experimentation were used. Since no significant difference was found between using attapulgite or bentonite, a bentonite poultice was prepared in the same manner discussed above. The top of plastic containers were cut to fit the tiles. The tiles were placed in the holes and the sides were sealed with paraffin wax. The container was filled with 600 milliliters of deionized water, to a height of approximately 4 centimeters, and the lid was sealed. The exposed surface of the tile was wetted with a spray of deionized water, the poultice was placed on the surface one centimeter thick. Finally the entire container was placed on a stand upside down. The rate of water evaporation from the poultice was greater than the rate of water migration through the tile; therefore, the poultice fell off from the tiles before all of the water could migrate through them. When the poultice fell off of the tile, the test was considered complete. All poultices fell off the tiles between nine and sixteen hours after the experiment began. The poultice was then dried and soaked in water as described above. The resulting solutions were then analyzed for salt content.

This technique showed a higher degree of efficiency of desalination than the simple poultice technique.

Table 22: Percent of Salt Removed with Pressure Poultice

| Tile | Salt | Previous Treatment | Percent of Salts Removed by Poultice |
|------|---|----------------------|--------------------------------------|
| E10 | NaCl Na ₂ SO ₄ | Intermittent Washing | 58% |
| E14 | NaCl Na ₂ SO ₄ | Intermittent Washing | 48% |
| S57 | NaCl Na ₂ SO ₄ | Intermittent Washing | 51% |
| S45 | NaCl Na ₂ SO ₄ | Intermittent Washing | 100% |

The calculated percentages are presented in Table 22. The results also show better removal of sulfate salts than the sodium chloride. This is best illustrated by comparing the ratio of chloride ions to sulfate ions in the tile to that measured in the poultice as shown in Table 23.

Table 23: Ratio of Sodium Chloride to Sulfate Salt Removed with Pressure Poultice

| Tile | Ratio of Salts Remaining | Ratio of Salts Removed During Poultice |
|--|--------------------------|--|
| E10 Sodium Chloride Sodium Sulfate | 3.3 | 1.1 |
| S57 Sodium Chloride Sodium Sulfate | 3.5 | 0.96 |

Only the values for the sodium chloride sodium sulfate mixtures are presented.

7. CONCLUSION

This study has served to evaluate the efficiency of various desalination methods from samples with known amounts of salt. Two sets of tiles with different porosities and impregnated with single salts and their mixtures were used. The salts chosen sodium chloride, sodium sulfate, and gypsum, alone or in their mixtures, are the most frequently found in both historic buildings and archaeological ceramics. The results obtained can be summarized as follows.

The removal efficiency does not appear to be affected by the amount of salts present originally in the material. In objects containing a single salt, the most soluble salts are the easiest to remove. In general, salts in mixtures are removed in the same ratio as they are present in the object.

The amount of water used for immersion does not influence the efficiency of salt removal. While long term immersion appears to remove virtually all the salts, the length of immersion time is not practical and may be damaging to the object.

Repeated washing does increase the efficiency of desalination, but the first washing always proves to be the most effective. Allowing objects to partially dry in between successive washings doubles the removal efficiency in subsequent immersions. Although this was proven for objects, the principle is applicable for in situ washing of buildings.⁷⁴

⁷⁴ G. Alessandrini, L.Toniolo, A. Antonioli, A. Di Silvestro, F. Piacenti, S. Righini Ponticelli and L. Formica. "On the Cleaning of Deteriorated Stone Materials," in *Conservation of Stone and Other*

As expected, the removal of salts from more porous materials is easier. However, salts such as mirabalite, sodium sulfate decahydrate, appear to concentrate in larger pores and hence were more effectively removed from the stoneware tiles during the first washing. Further studies are needed to elucidate the effect of pore size and shape on the accumulation of salt during crystallization. This may also influence the rate of removal of one salt preferentially to another.

Poulticing appears to be even more effective than one hour total immersion. Poulticing has also proven to be a more effective salt removal method for stoneware tiles than for earthenware tiles. Pressure poulticing significantly increases the efficiency of desalination.

Apart from evaluating the effectiveness of salt removal by various methods and their variations, this study may well serve as a guideline for estimating the amounts of salt remaining in a material, after one of these procedures is applied. Knowing the approximate efficiency of the technique and measuring the amount of salt removed from materials of similar porosity, the original salt content of the material can be estimated. This is an important contribution to the field of conservation. Since, as mentioned previously, no simple, accurate, and nondestructive method to determine salt content within porous materials exists.

APPENDIX A: SOLUBILITY OF COMMON SALTS FOUND IN BUILDINGS⁷⁵

| Chemical Formula | Name | Solubility g/100ml in cold water or (°C) | Molarity |
|---|----------------|---|------------------------|
| $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | Gypsum | 0.241 | 0.014 M |
| Na_2SO_4 | Thenardite | 4.76 (0°C) | 0.34 M |
| $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ | Mirabilite | 11 (0°C) | 0.34 M |
| K_2SO_4 | Arcanite | 12 (25°C) | 0.69 M |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | Epsomite | 71 (20°C) | 2.9 M |
| CaCl_2 | -- | 74.5 (20°C) | 6.7 M |
| NaCl | Halite | 35.7(0°C) | 6.1 M |
| KCl | Sylvite | 34.7 (30? °C) | 4.7 M |
| MgCl_2 | -- | 54.25 (20? °C) | 5.7 M |
| KNO_3 | Salt peter | 13.3 (0°C) | 1.3 M |
| NaNO_3 | Soda Niter | 92.1 (25°C) | 10.8 M |
| $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ | Brushite | 0.0316 (28? °C) | 0.0018 M |
| $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ | Hydromagnesite | 0.04 | 0.0011 M |
| Na_2CO_3 | -- | 7.1 (0°C) | 0.67 M |
| $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ | Thermonatrite | 33 | 2.7 M |
| $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ | Natron/Soda | 21.52 (0°C) | 0.72 M |
| CaCO_3 | Calcite | 0.0014(25°C) | 1.4×10^{-4} M |
| $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ | Trona | 13 (0°C) | 0.58 M |

⁷⁵ Robert C. Weast (ed.). "Physical Constants of Inorganic Compounds." *CRC Handbook of Chemistry and Physics 58th Edition*. (Cleveland: CRC Press, 1978), p. B-83-B178.

APPENDIX B: PORE MEASUREMENTS OF EARTHENWARE TILE

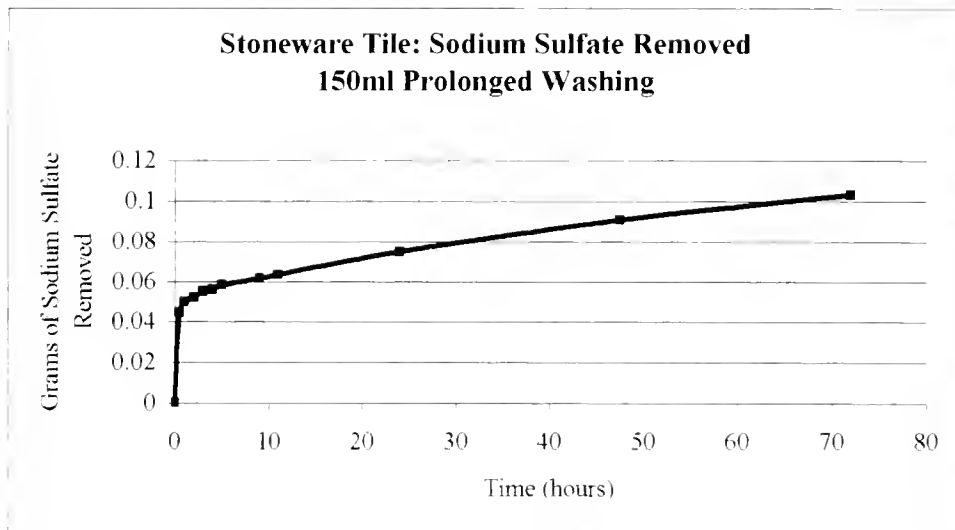
| Pore | Major Axis mm | Minor Axis mm | Area mm ² |
|--------------------|---------------|---------------|----------------------|
| 1 | 0.15 | 0.10 | 0.0491 |
| 2 | 0.17 | 0.10 | 0.0556 |
| 3 | 0.22 | 0.07 | 0.0504 |
| 4 | 0.08 | 0.05 | 0.0131 |
| 5 | 0.08 | 0.01 | 0.0026 |
| 6 | 0.03 | 0.02 | 0.0020 |
| 7 | 0.03 | 0.02 | 0.0020 |
| 8 | 0.03 | 0.02 | 0.0020 |
| 9 | 0.02 | 0.02 | 0.0013 |
| 10 | 0.03 | 0.01 | 0.0010 |
| 11 | 0.01 | 0.01 | 0.0003 |
| 12 | 0.02 | 0.01 | 0.0007 |
| 13 | 0.01 | 0.01 | 0.0003 |
| 14 | 0.01 | 0.01 | 0.0003 |
| 15 | 0.01 | 0.01 | 0.0003 |
| 16 | 0.09 | 0.02 | 0.0059 |
| 17 | 0.06 | 0.04 | 0.0079 |
| 18 | 0.03 | 0.02 | 0.0020 |
| 19 | 0.01 | 0.01 | 0.0003 |
| 20 | 0.06 | 0.04 | 0.0079 |
| 21 | 0.02 | 0.01 | 0.0007 |
| 22 | 0.03 | 0.02 | 0.0020 |
| 23 | 0.02 | 0.02 | 0.0013 |
| 24 | 0.01 | 0.01 | 0.0003 |
| 25 | 0.01 | 0.01 | 0.0003 |
| 26 | 0.01 | 0.01 | 0.0003 |
| 27 | 0.02 | 0.01 | 0.0007 |
| 28 | 0.01 | 0.01 | 0.0001 |
| 29 | 0.01 | 0.01 | 0.0001 |
| 30 | 0.01 | 0.01 | 0.0003 |
| Mean | 0.044 | 0.024 | 0.0033 |
| Median | 0.02 | 0.01 | 0.0007 |
| Standard Deviation | 0.054 | 0.026 | 0.015 |

APPENDIX C: PORE MEASUREMENTS OF STONEWARE TILE

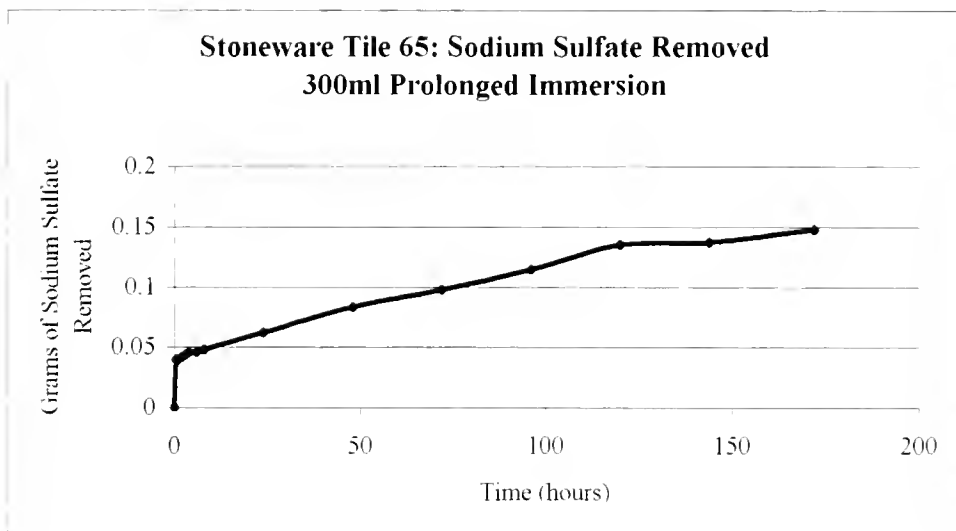
| Pore | Major Axis mm | Minor Axis mm | Area mm ² |
|--------------------|---------------|---------------|----------------------|
| 1 | 0.71 | 0.51 | 1.14 |
| 2 | 0.17 | 0.10 | 0.06 |
| 3 | 0.05 | 0.05 | 0.01 |
| 4 | 0.43 | 0.18 | 0.25 |
| 5 | 0.05 | 0.05 | 0.01 |
| 6 | 0.06 | 0.06 | 0.01 |
| 7 | 0.13 | 0.02 | 0.01 |
| 8 | 0.10 | 0.02 | 0.01 |
| 9 | 0.05 | 0.03 | 0.00 |
| 10 | 0.05 | 0.03 | 0.00 |
| 11 | 0.07 | 0.03 | 0.01 |
| 12 | 0.12 | 0.02 | 0.01 |
| 13 | 0.06 | 0.04 | 0.01 |
| 14 | 2.40 | 0.80 | 6.03 |
| 15 | 0.48 | 0.20 | 0.30 |
| 16 | 2.72 | 0.64 | 5.47 |
| 17 | 0.12 | 0.12 | 0.05 |
| 18 | 0.12 | 0.08 | 0.03 |
| 19 | 0.12 | 0.08 | 0.03 |
| 20 | 0.16 | 0.04 | 0.02 |
| 21 | 0.08 | 0.08 | 0.02 |
| 22 | 0.16 | 0.12 | 0.06 |
| 23 | 0.16 | 0.08 | 0.04 |
| 24 | 0.12 | 0.08 | 0.03 |
| 25 | 0.04 | 0.04 | 0.01 |
| 26 | 0.04 | 0.04 | 0.01 |
| 27 | 0.04 | 0.04 | 0.01 |
| 28 | 0.04 | 0.02 | 0.00 |
| 29 | 0.02 | 0.02 | 0.00 |
| 30 | 0.04 | 0.04 | 0.01 |
| Mean | 0.30 | 0.12 | 0.11 |
| Median | 0.11 | 0.05 | 0.02 |
| Standard Deviation | 0.63 | 0.19 | 1.46 |

APPENDIX D: ADDITIONAL DESALINATION GRAPHS AND TABLES

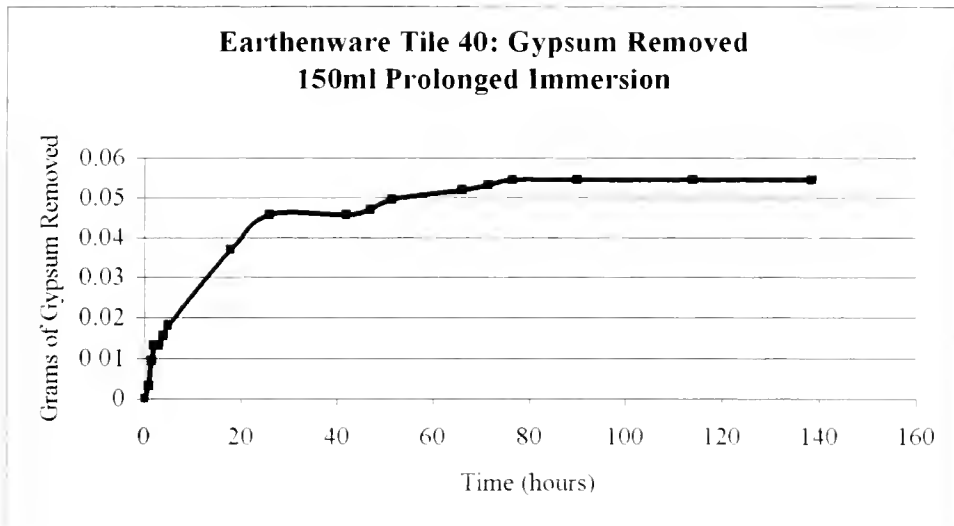
Graph D1: Grams of Sodium Chloride Removed During 150ml Prolonged Immersion of Earthenware Tile



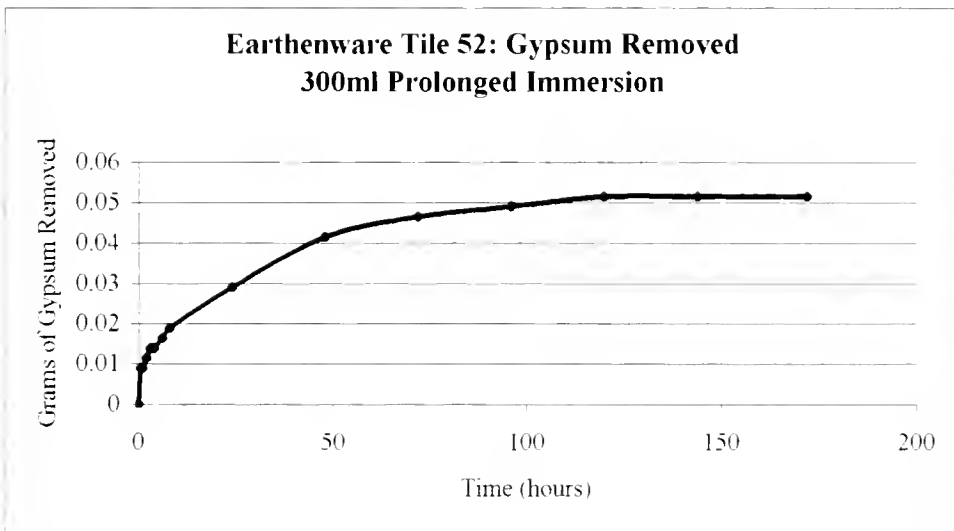
Graph D2: Grams of Sodium Chloride Removed During 300ml Prolonged Immersion of Earthenware Tile



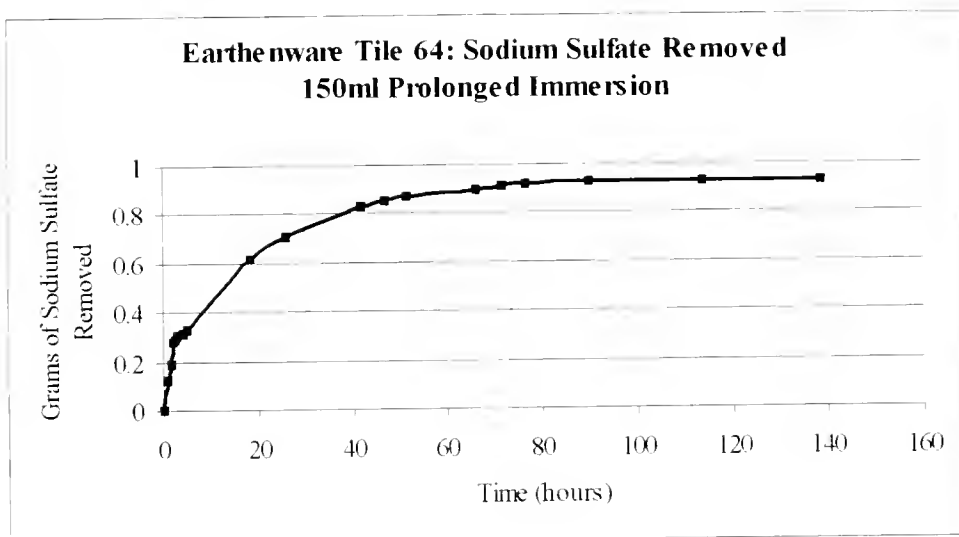
Graph D3: Grams of Sodium Chloride Removed During 150ml Prolonged Immersion of Stoneware Tile



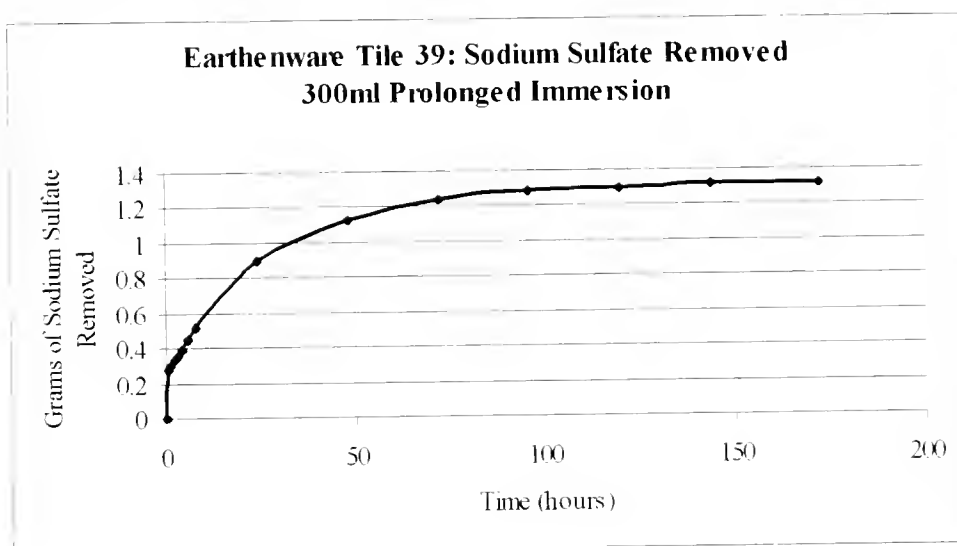
Graph D4: Grams of Sodium Chloride Removed During 300ml Prolonged Immersion of Stoneware Tile



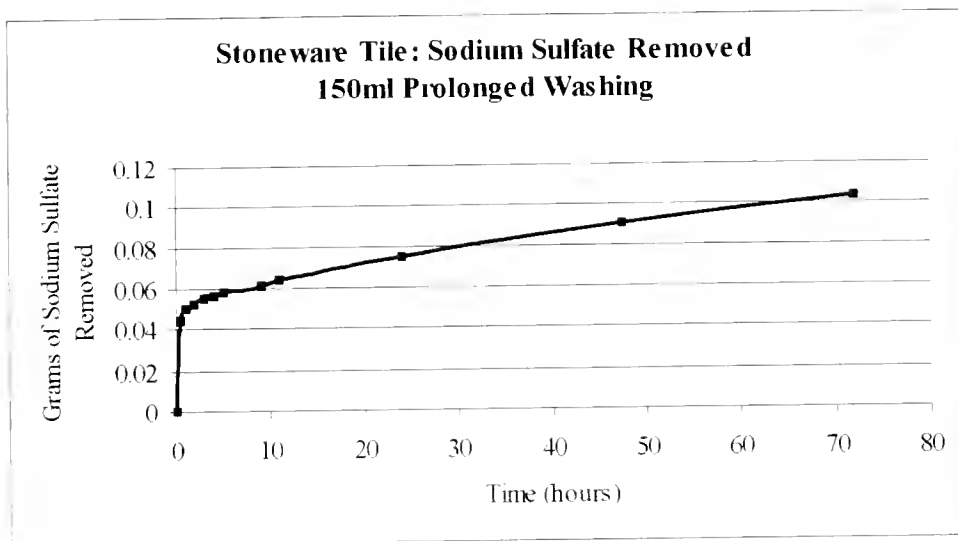
Graph D5: Grams of Sodium Sulfate Removed During 150ml Prolonged Immersion of Earthenware Tile



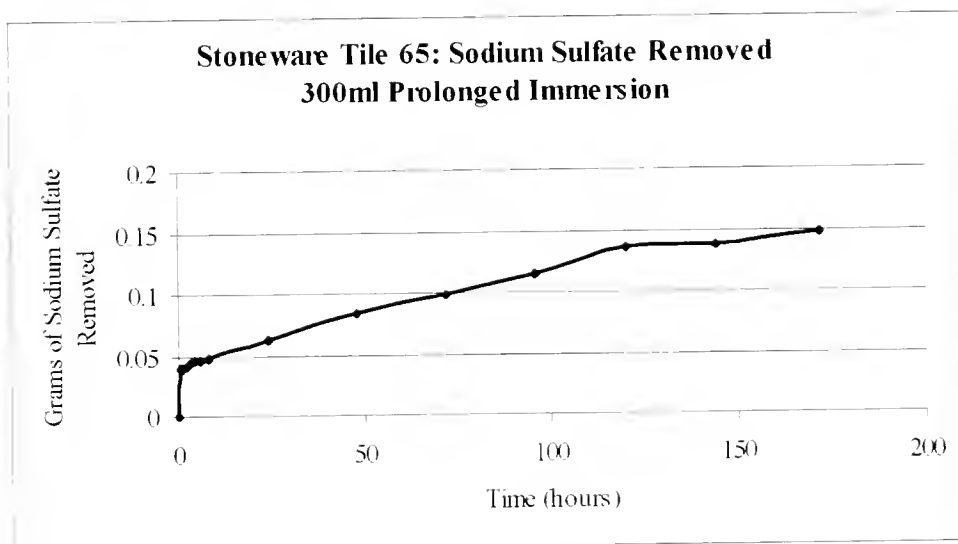
Graph D6: Grams of Sodium Sulfate Removed During 300ml Prolonged Immersion of Earthenware Tile



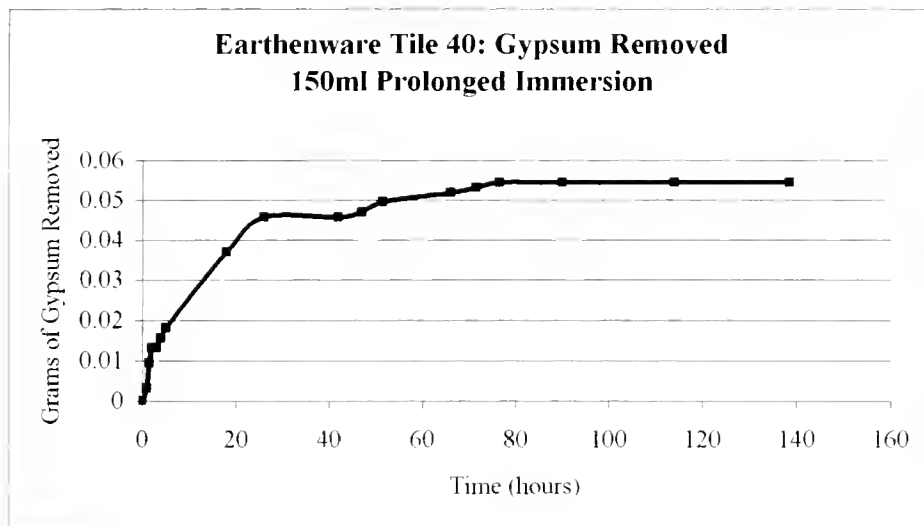
Graph D7: Grams of Sodium Sulfate Removed During 150ml Prolonged Immersion of Stoneware Tile



Graph D8: Grams of Sodium Sulfate Removed During 300ml Prolonged Immersion of Stoneware Tile



Graph D9: Grams of Gypsum Removed During 150ml Prolonged Immersion of Earthenware Tile



Graph D10: Grams of Gypsum Removed During 300ml Prolonged Immersion of Earthenware Tile

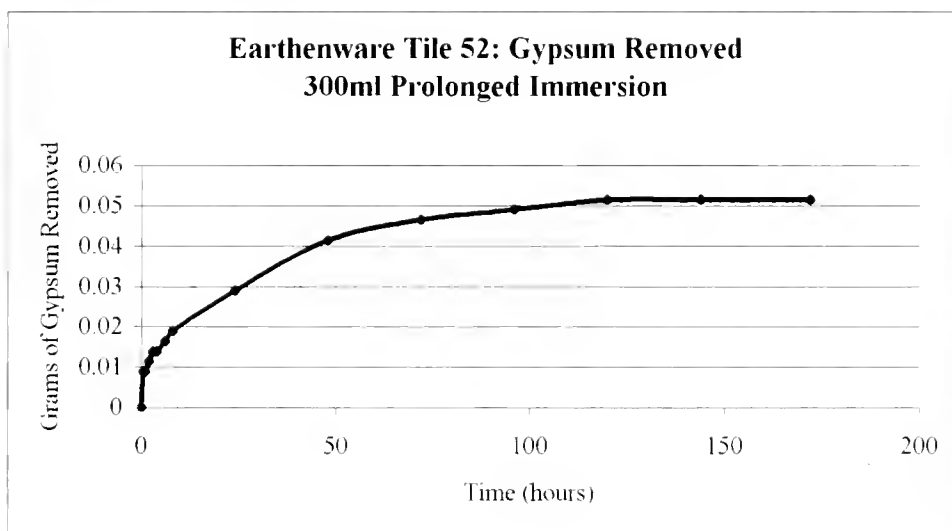


Table D1: Grams of Salt Removed During Intermittent Washings of Earthenware Tiles

| Tile | Salt | Calculated Amount of Salts (grams) | Grams of Salt Removed | | |
|------|---------------------------------|------------------------------------|-----------------------|---------------|---------------|
| | | | Sol.1 (grams) | Sol 2 (grams) | Sol 3 (grams) |
| E-10 | Total | 3.72 | 1.28 | 0.26 | 0.24 |
| | NaCl | 2.87 | 0.96 | 0.20 | 0.18 |
| | Na ₂ SO ₄ | 0.85 | 0.32 | 0.06 | 0.06 |
| E-26 | Total | 3.71 | 1.39 | 0.27 | 0.26 |
| | NaCl | 2.86 | 0.96 | 0.21 | 0.20 |
| | Na ₂ SO ₄ | 0.85 | 0.43 | 0.06 | 0.06 |
| E-72 | Total | 3.87 | 1.56 | 0.24 | 0.20 |
| | NaCl | 2.98 | 1.31 | 0.20 | 0.15 |
| | Na ₂ SO ₄ | 0.89 | 0.25 | 0.04 | 0.05 |
| E-43 | Total | 2.68 | 0.69 | 0.23 | 0.21 |
| | NaCl | 2.63 | 0.67 | 0.22 | 0.20 |
| | Gypsum | 0.05 | 0.02 | 0.005 | 0.005 |
| E-14 | Total | 2.53 | 0.59 | 0.29 | 0.25 |
| | NaCl | 2.48 | 0.58 | 0.28 | 0.25 |
| | Gypsum | 0.05 | 0.01 | 0.01 | 0.004 |
| E-30 | Total | 2.36 | 0.44 | 0.17 | 0.17 |
| | NaCl | 2.32 | 0.44 | 0.17 | 0.16 |
| | Gypsum | 0.04 | <0.002 | 0.002 | 0.008 |

Table D2: Grams of Salt Removed During Intermittent Washings of Stoneware Tiles

| Tile | Salt | Calculated Amount of Salts (grams) | Grams of Salt Removed | | |
|------|---------------------------------|------------------------------------|-----------------------|---------|---------|
| | | | Sol.1 | Sol 2 | Sol 3 |
| S-34 | Total | 1.36 | 0.17 | 0.04 | 0.04 |
| | NaCl | 1.05 | 0.11 | 0.03 | 0.03 |
| | Na ₂ SO ₄ | 0.31 | 0.06 | 0.01 | 0.01 |
| S-57 | Total | 1.36 | 0.17 | 0.05 | 0.06 |
| | NaCl | 1.05 | 0.12 | 0.04 | 0.05 |
| | Na ₂ SO ₄ | 0.31 | 0.05 | 0.01 | 0.01 |
| S-70 | Total | 1.41 | 0.16 | 0.05 | 0.05 |
| | NaCl | 1.09 | 0.11 | 0.04 | 0.05 |
| | Na ₂ SO ₄ | 0.32 | 0.05 | 0.005 | 0.004 |
| S-73 | Total | 0.74 | 0.19 | 0.02 | 0.02 |
| | NaCl | 0.73 | 0.18 | 0.02 | 0.02 |
| | Gypsum | 0.01 | 0.008 | <0.0002 | 0.002 |
| S-45 | Total | 0.76 | 0.154 | 0.03 | 0.06 |
| | NaCl | 0.75 | 0.15 | 0.01 | 0.06 |
| | Gypsum | 0.01 | 0.004 | 0.02 | 0.00 |
| S-29 | Total | 0.72 | 0.12 | 0.03 | 0.02 |
| | NaCl | 0.71 | 0.11 | 0.03 | 0.02 |
| | Gypsum | 0.01 | 0.008 | <0.0002 | <0.0002 |

Table D3: Grams of Salt Removed with Pressure Poultice

| Tile | Salt | Estimated Grams of Salt Remaining in Tile | Grams of Salts Removed by Poultice |
|------|---------------------------------|---|------------------------------------|
| E10 | Total | 1.94 | 1.13 |
| | NaCl | 1.53 | 0.58 |
| | Na ₂ SO ₄ | 0.46 | 0.55 |
| E14 | Total | 1.39 | 0.67 |
| | NaCl | 1.37 | 0.50 |
| | Gypsum | Not Detectable | Not Detectable |
| S57 | Total | 1.08 | 0.55 |
| | NaCl | 0.83 | 0.27 |
| | Na ₂ SO ₄ | 0.24 | 0.28 |
| S45 | Total | 0.51 | 0.52 |
| | NaCl | 0.53 | 0.30 |
| | Gypsum | Not Detectable | Not Detectable |

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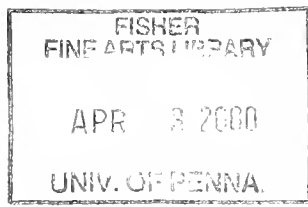
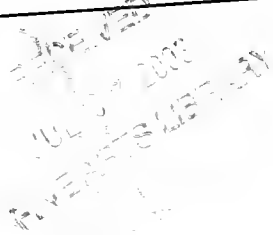
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